



# Nanoporous nickel-copper-phosphorus amorphous alloy film for methanol electro-oxidation in alkaline medium



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## ABSTRACT

Nanoporous Ni-Cu-P amorphous alloy (NP-NiCuP) and nanoporous Ni-Cu crystalline alloy (NP-NiCu) are prepared by the linear sweep voltammetry (LSV) etching of copper from the electroless Ni-Cu-P and Ni-Cu alloy coatings, respectively. The results of X-ray diffraction (XRD) analysis show that the nanoporous Ni-Cu-P alloy is amorphous structure. The scanning electron microscopy (SEM) analysis demonstrates the NP-NiCuP shows a 3-D bi-continuous porous structure with the pore size of 150–200 nm and the ligament size of around 100 nm. Electrochemical performances are measured by cyclic voltammetry (CV) and chronoamperometry (CA). The results prove that the NP-NiCuP electrode exhibits higher the proton diffusion coefficient ( $D_0$ ) of  $\text{Ni}(\text{OH})_2$  and surface coverage ( $\Gamma^*$ ) of the redox species than those on smooth electroless Ni-Cu-P amorphous alloy (S-NiCuP) and NP-NiCu electrodes in alkaline solution obviously. Moreover, electro-oxidation of methanol suggests that the NP-NiCuP electrode holds higher anodic current density and lower onset potential than the S-NiCuP and NP-NiCu electrodes. Finally, the NP-NiCuP electrode has stable redox behavior and superior catalytic stability for methanol oxidation.

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## 1. Introduction

The development of alternative power sources is an important issue at present. The direct methanol fuel cell (DMFC) is considered as an ideal choice for future energy resource due to availability, wide range of sources, low-cost, convenient storage and high energy density [1,2]. Electrocatalytic oxidation of methanol is a critical step in DMFCs, and developing new and efficient anode catalysts in DMFCs has received an enormous amount of attention [3–5]. While Pt [6,7] and Pt-based [8,9] catalysts are best-known materials for methanol electro-catalytic oxidation in the DMFCs, the commercialization of fuel cells is severely hampered by the high cost, sluggish kinetics, and low stability of the platinum catalysts.

Therefore, many efforts have recently been devoted to develop non-Pt materials for methanol oxidation such as Pd [8], Au [9], Ag [10] and Ni [11–13] catalysts. Among them, Ni catalyst shows relatively low cost, excellent electrochemical stability and resistance to poisoning, and its catalytic performance for methanol oxidation has been studied in alkaline medium since the 70's last century [14]. In order to get a better catalytic activity of Ni-based

catalysts for methanol oxidation, different morphologies and structures of Ni-based catalysts have been prepared. For instance, Shafei et al. [15] modified glassy carbon electrode with nickel hydroxide, Golikand et al. [16] reported a nickel electrode modified by nickel dimethylglyoxime, Wang et al. [17] modified electrode with Ni-Al layered double hydroxide film, Ding et al. [18] obtained highly ordered Ni-Cu alloy nanowire arrays, Enizi et al. [19] prepared  $\beta\text{-Ni}(\text{OH})_2\text{-NiCo}_2\text{O}_4$  hybrid nanostructure.

Recently, we prepared Ni-B amorphous alloy for alcohol oxidation [20–23]. Nickel-based amorphous alloy with the short-range order of atom clusters and long-range disorder structure, the absence of grain boundaries and dislocations in the amorphous structure result in a homogeneous and isotropic material down to the atomic scale [24], which display unique properties in comparison with crystalline materials, particularly high corrosion resistance and good catalytic activity. Previously, we have shown that Ni-based amorphous alloy have excellent alcohol oxidation activities [20–23]. In addition, amorphous alloy catalysts, such as Pd-Ni-Cu-P nanowires [25], Pt-Ni-Cu-P nanowires [26], Ni-Cu-P/C [27], Ni-B/TiO<sub>2</sub> [28], and Ni-B-graphene [29], have been prepared and presented significantly high electro-activity toward methanol, and ethanol oxidation. However, the investigators generally employed nickel-based amorphous alloy particles modified a conductive and corrosion-resistant substrate to improve active surface area. In such designs, amorphous alloy

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are usually absorbed to substrate weakly or tended to agglomerate over time under operational process, which lessening their active surface area and limiting working lifetime [30,31]. In this sense, we try to describe a new kind of material of nanoporous nickel-based amorphous alloy film.

Nanoporous materials regarded as not only an excellent scaffold material, but also a good catalytic material of anode electrode in DMFCs. Notably, there have been many studies on nanoporous single-element materials, such as nanoporous Pt [32], Pd [33], Cu [34], Au [35,36], Ag [37], Ni [38–40], which showed higher methanol catalytic performances as compared with the bulk materials. The nanoporous materials were generally formed by dealloying method, in which the less noble component A in a binary  $A_xB_{1-x}$  or multicomponent alloy is selectively removed by chemically or electrochemically [41]. To the best of our knowledge, there is less attention has been paid to develop nanoporous binary alloy [42,43], and there have not public report about 3-D bi-continuous nanoporous ternary amorphous alloy.

In the present work, we applied the linear sweep voltammetry (LSV) etching method to etching Ni-Cu-P alloy film to prepare the nanoporous Ni-Cu-P amorphous alloy material. The results show that the Ni-Cu-P amorphous alloy with fine 3D bi-continuous porous structure is obtained. As expected, the nanoporous NiCuP amorphous (NP-NiCuP) electrode has higher anodic current density, lower onset oxidation potential and better stability than the smooth Ni-Cu-P amorphous alloy film (S-NiCuP) and nanoporous Ni-Cu crystalline alloy (NP-NiCu) electrodes.

## 2. Experimental Section

### 2.1. Preparation of electrodes

Samples of low carbon steel plate ( $S=0.2\text{ cm}^{-2}$ ) used as the substrates for electroless Ni-Cu and NiCu-P films. Firstly, they welded on copper wire with a particularly sealed PTFE jacket and were then polished to mirror-like smoothness with metallographic abrasive paper (1200–1300 grain size). Thereafter in that order put into deionized water with ultrasonic for 8 min, chemical polishing solution of 10 wt.%  $\text{H}_2\text{SO}_4$ , 50 wt.% HCl and 40 wt.%  $\text{H}_2\text{O}$  for 20 s, deionized water and 10 wt.% HCl for 1 min. Finally, the resulting samples were carefully rinsed with doubly distilled water for further use.

The electroless Ni-Cu-P alloy film was synthesized by electroless plating method. The composition of the electroless plating solution was  $25\text{ g L}^{-1}$   $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ ,  $4\text{ g L}^{-1}$   $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ,  $60\text{ g L}^{-1}$   $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3\cdot \text{H}_2\text{O}$ ,  $20\text{ g L}^{-1}$   $\text{CH}_3\text{COONa}$  and  $25\text{ g L}^{-1}$   $\text{NaH}_2\text{PO}_2\cdot \text{H}_2\text{O}$ . The plating bath was adjusted to the pH value of 10 by 5 wt.% NaOH and the value of temperature at 356 K, and the deposition time was investigated about 15 min to achieve the optimum condition for the electroless plating process.

The NP-NiCuP electrodes were prepared by LSV etching from the electroless Ni-Cu-P alloy film samples. The LSV etching process was performed in a three-electrode cell with a platinum counter electrode and a saturated calomel reference electrode (SCE), and the electroless Ni-Cu-P alloy film sample as working electrode. The electrochemical etching solution contains 1 M  $\text{NiSO}_4$ , 0.01 M  $\text{CuSO}_4$  and 0.5 M  $\text{H}_3\text{BO}_3$ , and the value of pH was 4. The LSV etching was carried out at a scan rate of  $0.5\text{ mV s}^{-1}$  with the potential range from 0.05 V to 0.10, 0.13, 0.15, 0.18 and 0.20 V (denoted as  $E_1$ ,  $E_2$ ,  $E_3$ ,  $E_4$  and  $E_5$ , respectively) to prepare different samples, which were summarized in Table 1.

The NP-NiCu electrode was prepared by LSV etching from electroless Ni-Cu alloy sample. The LSV etching was carried out at a scan rate of  $0.5\text{ mV s}^{-1}$  with the potential range from 0.05 V to 0.15 V. The composition of the Ni-Cu alloy plating solution was  $25\text{ g L}^{-1}$   $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ ,  $0.1\text{ g L}^{-1}$   $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ,  $60\text{ g L}^{-1}$

**Table 1**  
Preparation of different electrodes.

| Electrode sample    | $E_e^a$ (V vs. SCE) | Electrode sample | $E_e^a$ (V vs. SCE) |
|---------------------|---------------------|------------------|---------------------|
| Ni-Cu-P alloys film | 0                   | NP-NiCuP-1       | 0.10 ( $E_1$ )      |
| NP-NiCuP-2          | 0.13 ( $E_2$ )      | NP-NiCuP-3       | 0.15 ( $E_3$ )      |
| NP-NiCuP-4          | 0.18 ( $E_4$ )      | NP-NiCuP-5       | 0.20 ( $E_5$ )      |
| S-NiCuP             | 0                   | NP-NiCu          | 0.15                |

<sup>a</sup> The LSV etching scanning ending potential.

$\text{C}_6\text{H}_5\text{O}_7\text{Na}_3\cdot \text{H}_2\text{O}$ ,  $20\text{ g L}^{-1}$   $\text{CH}_3\text{COONa}$  and  $4\text{ mL L}^{-1}$   $\text{N}_2\text{H}_4\cdot \text{H}_2\text{O}$ . The plating bath was adjusted to the pH value of 11 by 5 wt.%  $\text{NH}_3\cdot \text{H}_2\text{O}$  and the value of temperature at 363 K, and the deposition time was investigated about 15 min.

The S-NiCuP electrode was utilized as an electrode for comparison and synthesized by electroless plating method. The composition of the plating bath was same as that of the Ni-Cu-P alloy film electrode, except that the content of  $\text{CuSO}_4$  was 1 g/L.

### 2.2. Characterization and measurements

The microstructure and composition of samples were characterized by SEM (S-4800, HITACHI) and energy dispersive X-ray Spectrometer (EDS; Oxford, INCA), and XRD (D8, ADVANCE) for the analysis of crystal structure. The electrochemical characterization of NP-NiCuP electrode was carried out using CHI760E and PARSTAR2273 electrochemical workstation in 1 M KOH solution containing different methanol concentrations at 298 K. The NP-NiCuP electrode, platinum plate ( $S=2.25\text{ cm}^{-2}$ ) and SCE were used as working electrode, counter electrode and reference electrode, respectively. The solutions were prepared using deionized water and analytical pure, electrolyte was treated through high purity nitrogen to remove oxygen for 15 min before testing.

## 3. Results and discussion

### 3.1. The microstructure and composition of the samples

Electrochemical etching of Ni-Cu-P alloy film sample through LSV is listed in Fig. 1A from 0.05 V to 0.30 V at  $0.5\text{ mV s}^{-1}$ .  $E_1$ ,  $E_2$ ,  $E_3$ ,  $E_4$  and  $E_5$  in Fig. 1A represent LSV etching ending potentials for preparing different NP-NiCuP samples.

Fig. 1B shows the XRD patterns of the Ni-Cu-P alloy film samples before and after LSV etching treatment. As is Fig. 1B (curve a) shown, the strong peaks located around  $43.8^\circ$  and  $44.9^\circ$  are assigned to Ni-Cu-P alloy and the (110) plane of Fe, respectively [44]. Fig. 1B (curves b to f) show the XRD patterns of the samples with different LSV etching treatments, which indicate that the intensity of the Ni-Cu-P alloy diffraction peak weakened gradually with the increasing of etching ending potential. Moreover, the bread-like dispersion characteristic peak of amorphous alloy can be observed around  $43.8^\circ$  since LSV etching ending potential set as 0.15 V, indicating that the microstructure of the NP-NiCuP-3 is amorphous structure [45]. The main reason for this interesting phenomenon may be that the electroless Ni-Cu-P alloy film contain amorphous Ni-Cu-P alloy and crystalline copper, and the corrosion rate of amorphous Ni-Cu-P alloy is slower than that of crystalline copper, and hence the crystalline copper content of the Ni-Cu-P alloy reduces gradually along with etching ending potential rising, and amorphous Ni-Cu-P alloy leaves behind.

The EDX analyses of electrodes (Fig. S1 and Table S1 in the Supplementary Information) clearly show that the P contents of the NP-NiCuP-3, NP-NiCuP-4, NP-NiCuP-5 electrodes is 8.44 wt.%, 7.44 wt.%, 6.36 wt.%, respectively. Makhsoos [46] have reported that the microstructure of Ni-P alloy is controlled by P content and changes to amorphous once the P content is more than 7 wt.%.

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