

碳负载的 Pd-Cu-Fe (Pd-Cu-Fe / C) 催化剂是由 Pd²⁺ 部分刻蚀可调二元 Cu-Fe 合金模板 (Cu₉Fe₁, Cu₈Fe₂, Cu₇Fe₃) 的新策略制成的。与 Pd / C 催化剂相比, 由 Cu₉Fe₁, Cu₈Fe₂ and Cu₇Fe₃ 模板部分刻蚀所得的催化剂的阳极峰电位分别负移了 51 mV, 88 mV 和 110 mV。其中, 由 Cu₇Fe₃ 模板所制得的催化剂表现出很高的催化活性和稳定性。表明它是甲酸燃料电池的一个很好的催化剂候选物。本次实验研究使用了 X 射线衍射分析, 透射电子显微镜和电化学测量的方法对 Cu-Fe / C 三元催化剂进行了相关性质的分析。



齊魯工業大學
QILU UNIVERSITY OF TECHNOLOGY

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题目: 多元纳米复合材料的制备及其甲酸燃料电池应用研究

Preparation of Pd-based tri-metal nano-composites and its application in direct formic acid fuel cells

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Abstract in English

Carbon loaded Pd-Cu-Fe catalysts (Pd-Cu-Fe/C) were fabricated with a novel strategy of partly etching carbon loaded tunable binary Cu-Fe alloy templates (Cu_9Fe_1 , Cu_8Fe_2 , Cu_7Fe_3) with Pd^{2+} . Compared with Pd/C catalysts, the anodic peak potential at the catalysts started from Cu_9Fe_1 , Cu_8Fe_2 and Cu_7Fe_3 shifted toward negative value by 51 mV, 88 mV and 110 mV, respectively. Among them, catalyst started from exhibited the highest catalytic activity and a high stability which suggest the Cu_7Fe_3 template is a good candidate for the formic acid fuel cell. The characteristics of the Pd-Cu-Fe/C ternary catalysts were correlated using X-ray diffraction analysis, transmission electron microscopy, and electrochemical measurements.

Key words: Carbon based palladium catalyst; Formic acid oxidation; Fuel cell; Etching ; Ternary catalysts.

Abstract in Chinese

碳负载的 Pd-Cu-Fe (Pd-Cu-Fe / C) 催化剂是由 Pd^{2+} 部分刻蚀可调二元 Cu-Fe 合金模板 (Cu_9Fe_1 , Cu_8Fe_2 , Cu_7Fe_3) 的新策略制成的。与 Pd / C 催化剂相比, 由 Cu_9Fe_1 , Cu_8Fe_2 and Cu_7Fe_3 模板部分刻蚀所得的催化剂的阳极峰电位分别负移了 51 mV, 88 mV 和 110 mV。其中, 由 Cu_7Fe_3 模板所制得的催化剂表现出很高的催化活性和稳定性。表明它是甲酸燃料电池的一个很好的催化剂候选物。本次实验研究使用了 X 射线衍射分析, 透射电子显微镜和电化学测量的方法对 Cu-Fe / C 三元催化剂进行了相关性质的分析。

关键词: 碳负载钯催化剂; 甲酸氧化; 燃料电池; 刻蚀; 三元催化剂。

Chapter 1. Introduction

1.1 Characteristics of Fuel cells

Fuel cells [1-5] is efficient, convenient and environmentally friendly green energy devices. In today's society, improving energy efficiency, reducing environmental pollution, are urgent need to solve the major problems. Fuel cell is a kind of device which is used for transferring the chemical energy of fuel and oxidizing agent directly into electrical energy through electrode reaction[6], with the characteristics of fuel diversification, exhaust clean, low noise and less pollution to the environment. Due to the reaction process does not involve burning. Accordingly, its energy conversion rate is not limited by carnot cycle, as high as 60%~80%. Fuel cells have several advantages compared with the traditional energy [7, 8]. (1) high efficiency, decentralized power generation device. (2) clean and safe power generation device.(3) “the power and waste heat utilization system” can be used at the same time (4) power generation environment friendly.(5) high flexibility, wide application, convenient and safe operation, etc. Fuel cells can be used in more places because of its simple structure. Generated Power depends on the number of single battery power and battery;

1.2 The advantages of direct formic acid fuel cells

Direct formic acid fuel cell (DFAFC) has many advantages [9-11]. Formic acid can be used as an additive to food and medicine, it is a non-polluting environmentally friendly material, formic acid is not flammable, safe for storage and transportation. Formic acid is a strong electrolyte which can promote the transmission of electrons and protons。 It is conducive to increasing the solution proton conductivity of anode roobm and formic acid can be ionized into formate, formate and Nafion membrane in the sulfonate mutual Rejection,

which partially hinders the transmission of formic acid, the permeability formic acid on the Nafion membrane is only 1/5 of methanol , so the low transmittance of formic acid can improve the efficiency of the battery. It's conducive to manage and allow the use of high concentrations of formic acid. The use of formic acid as fuel is very suitable mobile power for use at room temperature or low temperature. Because of the formic acid with high energy conversion efficiency, low permeability of formic acid, non-toxic, non-flammable, etc.

1.3 The working principle and structure of direct formic acid fuel cell (DFAFC)

Direct formic acid fuel consist of anode, cathode, proton exchange membrane and bipolar plate . The working principle is as follows:

Anode:



Cathode:

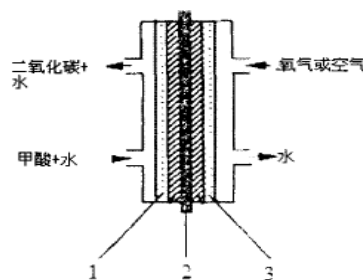


The total battery reaction is:



Direct formic acid fuel cell works as shown in Figure 1-1: formic acid is oxidized to produce CO₂ on the anode, electrons and protons was released at the same time, electrons from the external loop through the load conduction to the cathode, while hydrogen protons through the electrolyte to the cathode. On the cathodes, electrons and protons react with oxygen, which is electrochemically reduced to water and consumes electrons and protons.

The structure is as follows:



1-anode 2-proton exchange membrane 3-cathode

Figure 1-1 DFAFC structure diagram

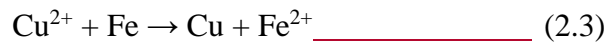
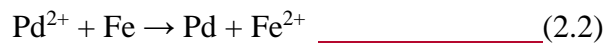
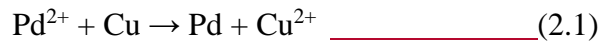
Charpter 2 Experimental

2.1 Introduction of Experimental part.

With hydrogen and light hydrocarbons as the fuel of the proton exchange membrane fuel cell has become an important technology of the next generation of power systems [12]. However, direct formic acid fuel cells with formic acid as a fuel for its good safety and environmental protection has become a powerful alternative for portable electronic devices [13, 14]. Formic acid has the advantages characteristics of safe, non-toxic, nonflammable and transportation convenient. The Nafion membrane permeability of formic acid is far lower than that of methanol [15] Because of the repulsive force between HCOO^- and SO_3^- ions. The research of electric catalytic oxidation catalyst of formic acid has been for a half century [16-17]. The are platinum catalyst [18] and palladium catalysts among them[19]. In the field of electrochemical catalysis, Pd is a very important metal [20-22]. Especially for formic acid oxidation, Pd and pt showed high catalytic activity and low toxicity of CO [23-25].People have explored some methods to improve the catalyst performance and and reduce consumption of Pd. Among them,one of the effective method is to change the composition of catalyst. Such as form binary and ternary Pd catalysts by joining the proper metal, such as Pd, Ag [22], Pd - Ni [23], Pd, Co, Pd - Co - Ir [24], etc.

Compared with the binary catalysts, ternary catalysts have much more elements and microstructure. With the increase of elements composition of catalysts, we can get quite a lot different kinds of catalysts. Thus, we need to prepare many samples for screening test. In this case, the experiment's work is very difficult. At present, Pd-Cu and Pd-Fe have been reported for the oxidation of formic acid. Cu and Fe and their alloys are essential for people's daily life and industrial production, and are well-stocked and inexpensive. We attempted to prepare Pd-Fe-M or Pd-Cu-M (M is a doped third metal). One of the easiest ideas is the simplest preparation of Pd-Cu-Fe ternary catalyst.

There are many methods for preparing multivariate catalysts, such as etching, alloying, electrodeposition, etc. [43-45]. Etching method has been applied more than ten years [46-48]. The etching process is usually carried out by a displacement reaction. In this way, a series of multifunctional, well-controlled hollow, porous structures and multicomponent heterogeneous structures with adjustable composition can be obtained [49]. In addition to the use of Pd²⁺ partial or total corrosion of Cu to prepare a monovalent palladium-based electrocatalyst [18] or a binary palladium-based electrocatalyst [50], we have developed a method for the preparation of ternary Pd- Catalyst method. According to the preparation principle, at least one metal in the alloy needs to be reduced by Pd²⁺. In this paper, the Pd-Cu-Fe / C catalyst was prepared by partially etching the Cu-Fe alloy via Pd²⁺. The etch process has at least the following process:



After etching for several hours, more than half of the atoms in the alloy are replaced by Pd atoms, so the resulting samples exhibit the catalytic performance of a typical Pd-based catalyst. Since the etching is not complete, the performance of the resulting catalyst is partially affected by the template. Through the simple preparation method, we obtain the complex multi-catalyst, these catalysts have good catalytic activity for formic acid oxidation and a certain stability.

Compared with the Pd/C catalyst, the anode potential of the Pd-Cu-Fe ternary catalyst is obviously negatively shifted, which shows a high catalytic activity. Among them, the Pd-Cu-Fe ternary catalyst prepared by Cu₇Fe₃/C template is negatively shifted by 110 mV than the Pd/ C_{peak} potential. The catalytic activity of these ternary catalysts is higher than that of binary catalysts, such as Pd₂Co [31], Pd_{0.97}Co_{0.03} [51], Pd_{0.8}Cr_{0.2} [52], compared to the peak potential of binary catalysts in some literature and the previously mentioned Pd-Cu and Pd-Fe catalysts. The negative shift of formic acid of the Pd-Cu-Fe/C catalyst obtained by etching the Cu₇Fe₃/C template from Pd²⁺ is 110 mV which is similar to that of 140 mV of the ternary Pd₄Co₂Ir/ C. Pd₄Co₂Ir catalyst is known to have the greatest displacement of formic acid electrocatalytic oxidation peaks. Cu, Fe is the most widely used and most readily

available metal. Cu and Cu alloys have good mechanical properties, such as excellent corrosion resistance and thermal conductivity [53]. Fe is one of the most commonly used metals in modern industry and is the most abundant metal on earth. The relative stability of Fe-based alloys is due to magnetic interactions [54]. Cu-Fe alloys are widely used in electronic components due to their strong electrical conductivity and low cost [55]. The preparation of this catalyst can also be extended to more electrochemical reactions, such as ethanol oxidation, oxygen reduction and so on.

2.2 Experimental part

2.2.1 Experimental device

Table 2-1 Experimental equipment and manufacturers

Instrument name and model	Manufacturer
Electrochemical analyzer (CHI832B)	Shanghai Chen Hua Instrument Company
Electronic balance (FA1004N type)	Shanghai Precision Science Instrument Co., Ltd
Ultrasonic cleaning machine (KQ-50B type)	Kunshan City ultrasound Instrument Co., Ltd.
Vacuum drying oven (DZF-6020)	Gong Yi City Yuhua Instrument Co., Ltd.
Rotary vane vacuum pump (2XZ-1 type)	Zhejiang Huangyan Ningxi Medical Equipment Co., Ltd
X-ray diffractometer (D8advance type)	Germany bruker-axs company
Transmission electron microscopy (JEM-2010F)	Japan Electronics Co., Ltd. (JEOL) company
X-ray photoelectron spectroscopy (XSAM-800)	Kratos, Japan
Inductively Coupled Plasma Emission	American PE company

Spectrometer (Optima 2000DV)

Scanning Electron Spectrometer (Octane EDAX company

Pro Silicon Drift (SDD) Detector)

Table 2-2 Reagents and drugs used in the experiment

name	Chemical formula	Manufacturer	purity
Activated carbon	Vulcan XC-72R	United States Cabot Corporation	
Palladium chloride	PdCl ₂	Chinese medicine Chemical reagents	analytical grade
Anhydrous copper sulfate	CuSO ₄	Shanghai Qiang Shun Chemical Reagent Co., Ltd.	analytical grade
Ferrous sulfate	FeSO ₄ ·7H ₂ O	Shanghai Shanhai Mission Experimental Plant	analytical grade
Sodium borohydride	NaBH ₄	Shanghai layer cloud Chemical Co., Ltd.	analytical grade
Anhydrous ethanol	C ₂ H ₅ OH	Chinese medicine Chemical reagents	analytical grade
Sodium hydroxide	NaOH	Chinese medicine	analytical grade

			Chemical reagents
Nafion solution	5% Nafion	United States	analytical grade
		DuPont company	
sulfuric acid	H ₂ SO ₄	Laiyang	fine analytical grade
		chemical plant	
hydrochloric acid	36% HCl	Tianjin	analytical grade
		Guangcheng	
		Chemical Reagent	
Formic acid	HCOOH	Chinese medicine	analytical grade
		Chemical reagents	

2.2.2 Preparation of catalyst

The preparation of carbon-supported ternary catalysts is shown in Figure 2.1.

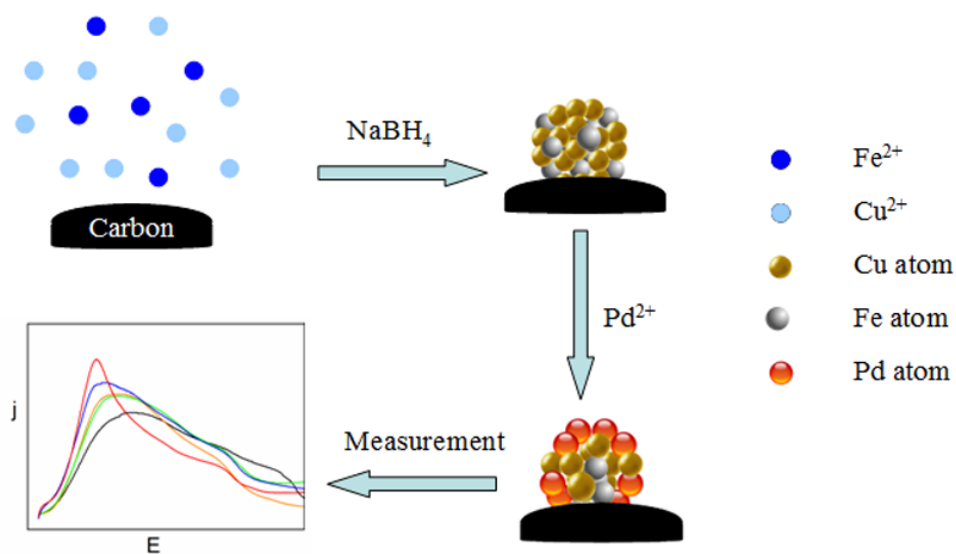


Figure 2.1 synthesis process of Pd-Cu-Fe/C ternary catalyst

The carbon supported Cu-Fe alloy template was prepared by the sodium borohydride reduction method we had used before [52, 56]. CuSO_4 and FeSO_4 were used as precursors of Cu and Fe, respectively. The atomic ratios of Cu and Fe in Cu and Fe alloys are Cu: Fe = 10: 0, 9: 1, 8: 2 and 7: 3, respectively.

The alloy template was etched in a 20 mmol L^{-1} PdCl_2 solution at room temperature for 3 hours. The PdCl_2 solution was formulated with 0.2 mol L^{-1} HCl. Adjust the pH to about 7 before use. The catalyst was filtered and washed thoroughly with three times distilled water. Finally, The catalyst was vacuum dried at 130°C for 6 hours. For ease of discussion, the catalysts obtained by etching $\text{Cu}_{10}\text{Fe}_0$, Cu_9Fe_1 , Cu_8Fe_2 and Cu_7Fe_3 are named $\text{NPCu}_{10}\text{Fe}_0$, NPCu_9Fe_1 , NPCu_8Fe_2 and NPCu_7Fe_3 , respectively. The Pd / C catalyst was prepared using sodium borohydride reduction. PdCl_2 is a precursor of Pd. The method of washing and drying is the same as the above-mentioned ternary catalyst .

2.2.3 Electrochemical test method

All electrochemical tests were performed in a three-electrode system by CHI832B electrochemical workstation. High purity carbon rod serve as the Counter electrode, Hg/HgSO_4 electrode as the reference electrode. 10 mg of the catalyst powder was added to 0.5 mL of ethanol and 0.5 mL of water, and the 20 minutes' ultrasound for forming a homogeneous suspension. $20 \mu\text{L}$ ($5 \mu\text{L} \times 4$ times) suspension was added dropwise to a 3 mm diameter glassy carbon electrode surface. The glassy carbon electrode was polished with $0.05 \mu\text{m}$ Al_2O_3 powder before use and rinsed with three times distilled water. After the catalyst was dried naturally, $2 \mu\text{L}$ of Nafion solution (5wt%) was added dropwise to the electrode. Cyclic voltammetry was performed in 0.5 mol L^{-1} H_2SO_4 solution. The linear sweep voltammetry curve and the time current curve were carried out in 0.5 mol L^{-1} H_2SO_4 and 0.5 mol L^{-1} HCOOH solution. The potentials in this paper are converted to standard hydrogen electrodes. The electrolyte solution was purged with N_2 for 20 minutes before testing, and the electrolyte was kept in the N_2 atmosphere during the test.

2.3 Results and discussion.

2.3.1 Characterization of the catalyst.

Figure 2.2 shows the XRD patterns of Pd-Cu-Fe/C and Pd/C catalysts. In the figure, the peak of about 24.8° on the spectrum of all the catalysts is the peak of C(002). (111), (200), (220) and (311) planes of Pd are about 40° , 46° , 68° and 82° , respectively. There is a relatively slow diffraction peak of Cu_2O near 35° [51]. No peaks on the Fe element were found in the figure, and this phenomenon also appears in some Pd-Fe electrocatalysts report[41, 57-58]. They point out that this is due to the heavy atom effect of Pd [41, 59], which forms Pd-coated Fe nanoparticles. The Pd-Cu-Fe catalyst is more complex than the binary catalyst, and the partially dissolved Cu^{2+} can be reduced by Fe on the surface. The catalyst was dried at 130°C , Pd, Cu, Fe three elements will spread each other, forming Pd-Cu-coated Cu-Fe nanoparticles of the boundaries are not obvious in the layers Pd-Cu and Cu-Fe. The linear position in the graph is the position of the diffraction peak of Pd in the Pd/C catalyst. The movement of the Pd peak position also indicates the formation of the alloy. The particle diameters of the particles can be calculated from the Hiller formula[60]. The calculated diameters of Pd/C, $\text{NPCu}_{10}\text{Fe}_0$, NPCu_9Fe_1 , NPCu_8Fe_2 and NPCu_7Fe_3 catalysts are 5.0 nm, 4.9 nm, 4.4 nm, 4.8 nm and 4.5 nm, respectively.

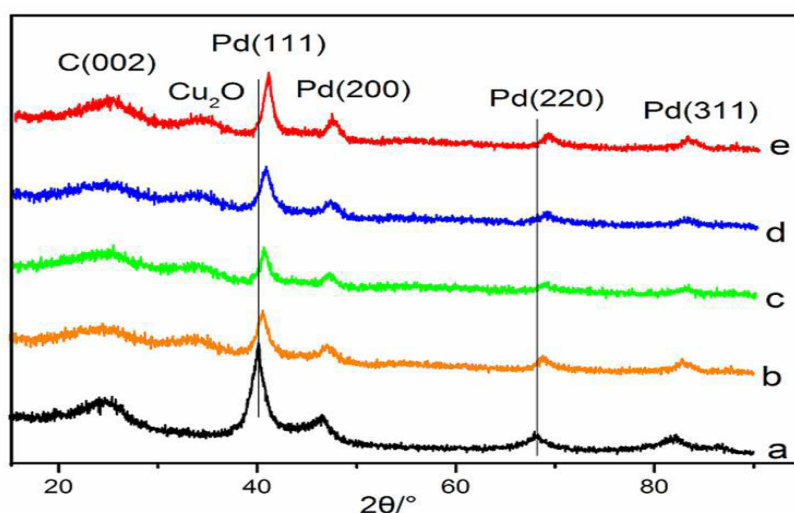


Figure 2.2 The XRD pattern of (a) Pd / C, (b) NPCu₁₀Fe₀, (c) NPCu₉Fe₁, (d) NPCu₈Fe₂ and (e) NPCu₇Fe₃. The straight line is the diffraction peak position of Pd in Pd/C catalyst.

2.3.2 Electrochemical test and morphology analysis of the catalyst.

Figure 2.3 shows the cyclic voltammograms of Pd-Cu-Fe/C and Pd/C catalysts in 0.5 mol L⁻¹ sulfuric acid. The peak in the range of 0 to 0.4 V is the desorption peak of hydrogen, and the peak after 0.5 V is the oxidation of the metal and the reduction peak of the oxide. The current density in the electrochemical curve is based on the electrochemically active area. The desorption peak of hydrogen is usually used to calculate the electrochemically active area [62-63]. However, since hydrogen easily enters the lattice of Pd, it becomes difficult to calculate the electrochemically active area using the desorption peak of hydrogen [64]. In this paper, the electrochemical active area is calculated by the reduction peak of Pd oxide [65]. The charge density of single layer PdO is 424 $\mu\text{C cm}^{-2}$. The electrochemical active area of the Pd-based catalyst can be obtained using the following formula [66]

$$\text{ECSA} = Q_{\text{R}} / Q_{\text{MR}} \quad (2.4)$$

Q_{R} is the reduced power of PdO, obtained by the reduction peak of PdO in the cyclic voltammogram in the sulfuric acid. Q_{MR} is a single layer PdO with a charge density of 424 $\mu\text{C cm}^{-2}$.

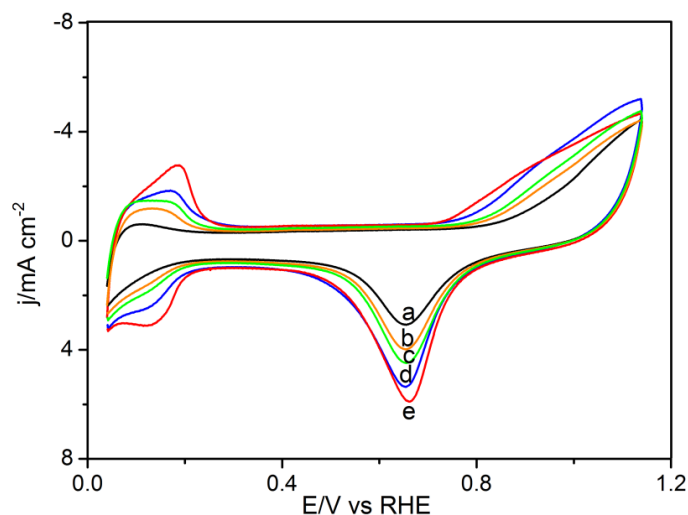


Figure 2.3 The cyclic voltammetry curves of (a) Pd/C, (b) NPCu₁₀Fe₀, (c) NPCu₉Fe₁, (d) NPCu₈Fe₂ and (e) NPCu₇Fe₃ catalysts in the solution of 0.5 mol L⁻¹ H₂SO₄. Scan speed 10 mV s⁻¹

The electrochemical properties were observed by linear scanning voltammetry curves of catalyst in 0.5 mol L⁻¹ HCOOH and 0.5 mol L⁻¹ H₂SO₄ solution. Figure 2.4 shows the linear scanned voltammograms of each catalyst in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH solution. It can be seen that there is a large peak in the range of 0.2-0.4 V. There is an indistinct slow peak in the range of 0.7-0.9 V. The peak in the range of 0.2-0.4 V is a direct oxidation peak of formic acid, which does not have CO toxicity. The peaks at 0.7-0.9 V are attributed to the oxidation of CO. The CO accumulated in the process of formic acid oxidation may be derived from the indirect oxidation of formic acid or the reduction of surface-generated CO₂. Based on the formation of CO in the electrooxidation of formic acid on Pd-based catalysts, some scientists have carried out spectroscopic studies. These spectroscopic studies [96-98] show that the reduction of CO₂ from formic acid dehydrogenation is the main source of CO. However, some literature suggests that the oxidation of formic acid through both the direct route and the CO pathway [23-34, 37, 70]. Based on the theory in the literature, we believe that part of the CO is obtained by the reduction of CO₂ from the oxidation product of the formic acid, since Ojani [39] pointed out that the oxidation of formic acid on the Pd-Cu porous catalyst produces CO intermediates by dehydration. The peak potential of NPCu₇Fe₃, NPCu₉Fe₁, NPCu₉Fe₁ and NPCu₁₀Fe₀ catalysts were negative shift by 110 mV, 88 mV, 51 mV and 46 mV, respectively, and the current densities were 48.3%, 27.9%, 15.6% and 17.2% higher than that of Pd/C. The peak of the NPCu₇Fe₃ catalyst is sharp, indicating that there are more accessible active sites on the catalyst [71]. The NPCu₇Fe₃ catalyst exhibits the highest catalytic activity in some catalysts.

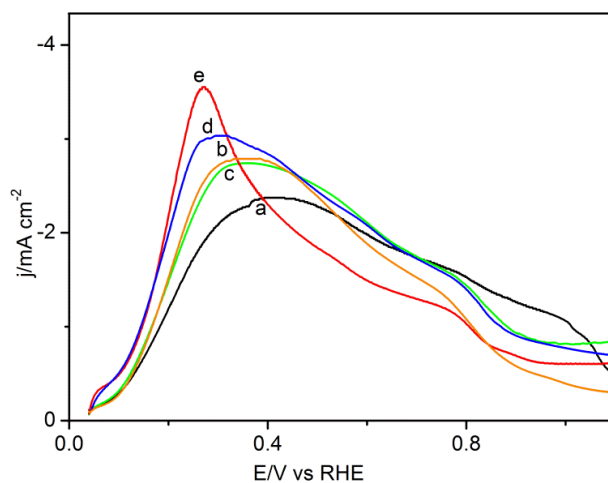


Figure 2.4 the Linear scan voltammetry curve of (a) Pd / C, (b) NPCu₁₀Fe₀, (c) NPCu₉Fe₁, (d) NPCu₈Fe₂ and (e) NPCu₇Fe₃ catalyst in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH solution ; scan speed: 10 mV s⁻¹

Figure 2.5 shows the time current curves for the Pd / C and NPCu₇Fe₃ catalysts in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH solution at an operating voltage of 0.3 V. The stable current density of NPCu₇Fe₃ catalyst is higher than that of Pd/C, which indicates that it has high stability.

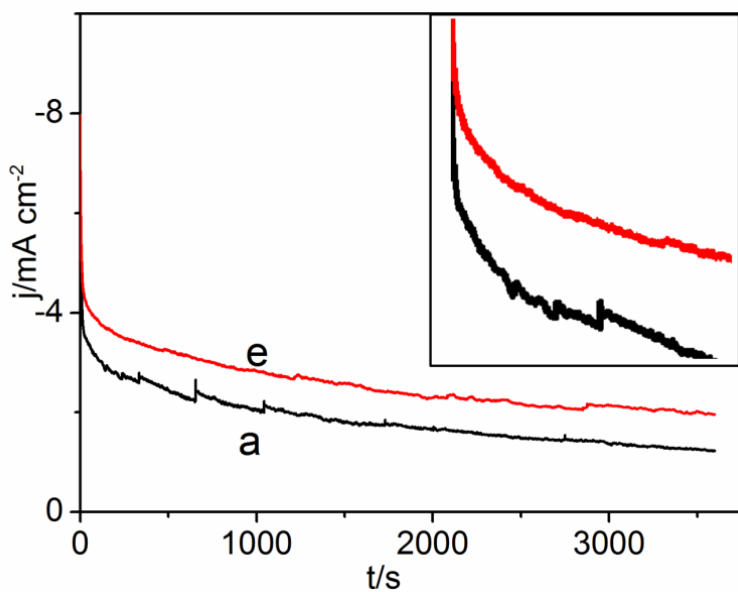


Figure 2.5 Time-current curves for Pd/C and NPCu₇Fe₃ catalysts; voltage: 0.3 V

2.4 Conclusion

In general, Pd-Cu-Fe/C ternary catalysts can be prepared by partial etching of alloy . The resulting ternary catalyst has a higher catalytic activity of formic acid. The Pd-Cu-Fe/C catalyst obtained from Cu₇Fe₃/C template exhibits the highest catalytic activity. [72]

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