[Article ID] 1003－6326(2002)06－1015－05

Preparation and electrocatalytic properties of tungsten carbide electrocatalysts①

MA Chun-an(马淳安)[1,2], ZHANG Wen-kui(张文魁)[1],
CHEN Dan-hong(成旦红)[2], ZHOU Bang-xing(周邦新)[2]
(1. Department of Applied Chemistry, Zhejiang University of Technology, Hangzhou 310014, China;
2. Department of Materials Science and Technology, Shanghai University, Shanghai 200072, China)

[Abstract] The tungsten carbide(WC) electrocatalysts with definite phase components and high specific surface area were prepared by gas-solid reduction method. The crystal structure, phase components and electrochemical properties of the as-prepared materials were characterized by XRD, BET(Brunauer Emmett and Teller Procedure) and electrochemical test techniques. It is shown that the tungsten carbide catalysts with definite phase components can be obtained by controlling the carburizing conditions including temperature, gas flowing rate and duration time. The electrocatalysts with the major phase of W_2C show higher electrocatalytic activity for the hydrogen evolution reaction. The electrocatalysts with the major phase of WC are suitable to be used as the anodic electrocatalyst for hydrogen anodic oxidation, which exhibit higher hydrogen anodic oxidation electrocatalytic properties in HCl solutions.

[Key words] tungsten carbide; electrocatalyst; electrochemical performance
[CLC number] TF 123.7; O 646.542 [Document code] A

1 INTRODUCTION

Since the discovery of the catalytic activity of tungsten carbide for hydrogen ionization in acid solutions by Böhm et al[1] in 1968, an increasing interest has drawn in the uses of tungsten carbides in catalysis and many results have been achieved. Subsequently, Boudart et al[2] found that tungsten carbide(WC) displayed "platinum-like" behavior in several reactions and this behavior of WC is dependent upon the chemical status of the surface carbon. Tungsten carbide was also found to compare favorably with platinum as an electrode for the oxidation of hydrogen[3]. From then on, more and more studies have been carried out on the catalytic properties of tungsten carbides, and the results have disclosed that tungsten carbides are active phases for many catalytic reactions[4~8] like carbon monoxide hydrogenation, hydrogen oxidation, hydrogen and methanol electro-oxidation, ammonia synthesis, hydrogenolysis and isomerization of hydrocarbons, carbon monoxide, nitric oxide and conversion of hydrocarbons from automobile exhaust gas etc. The previous works have shown that tungsten carbide exhibits high electrocatalytic activity for hydrogen ionization in sulfuric acid and phosphoric acid electrolyte[9]. By using H_3PO_4 as electrolyte, Pt as cathode and WC as anode, Böhm et al[1] fabricated H_2-O_2 fuel cell stacks and the continuous run lifetime reached to 5 000 h in 150 ℃. Maas[10] also manufactured the H_2-O_2 fuel cell stacks with the output power up to 1 kW, and the properties of the as-prepared fuel cell stack was still stable after long time run.

Using chlorine as oxidant and appropriate electrocatalysts, H_2-Cl_2 fuel cell can be established. Unlike H_2-O_2 fuel cell, the reactant of H_2-Cl_2 fuel is HCl, a widespread useful fundamental chemical raw product. So this fuel cell has potential applications in chemical factory to co-produce electricity and useful HCl product as well.

The aim of the present work is to prepare tungsten carbides with high stability and high electrocatalytical activity and suitable for hydrogen oxidation electrodes in H_2-Cl_2 fuel cells. In this paper, the preparation and electrocatalytical properties of the tungsten carbide electrodes in different electrolyte solutions are reported.

2 EXPERIMENTAL

Tungsten carbide electrocatalysts were prepared by reduction of yellow modification of H_2WO_4 under the flowing CO(99.9% in purity) and CO_2(99% in purity) mixture with $\varphi(CO)/\varphi(CO_2) \approx 1:10$. The initial raw material of yellow H_2WO_4 was supported on a ceramics boat in a quartz synthesis reactor. The schematic flow diagram is shown in Fig. 1. The flow rates of CO_2 and CO mixture were about 48 mL/(h·g) H_2WO_4 and

① [Foundation item] Project(200024) supported by the Natural Science Foundation of Zhejiang Province, China; project(20276069) supported by the National Natural Science Foundation of China
[Received date] 2002－02－26; [Accepted date] 2002－05－08

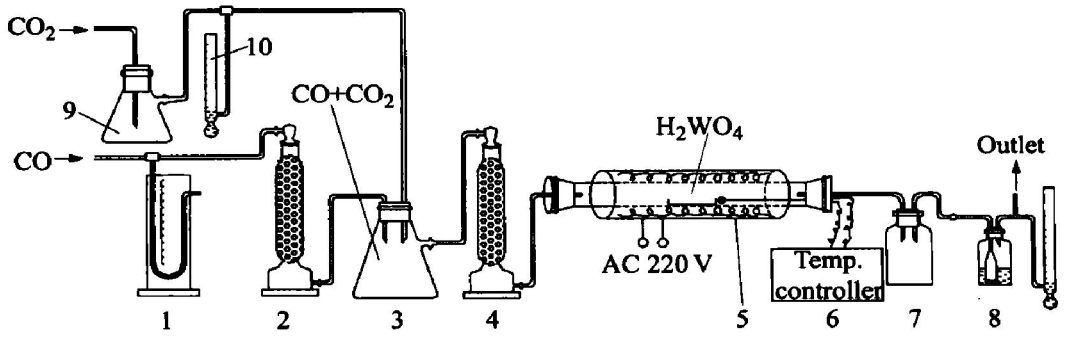

Fig. 1 Schematic flow diagram of preparation of WC electrocatalyst
1—Pressure gauge; 2—Gas drier; 3—Gas mixer; 4—Gas drier; 5—Reactor; 6—Temperature controller; 7—Buffer bottle; 8—Absorber; 9—Buffer bottle; 10—Gas indicator

about 480 mL/(h·g) H_2WO_4, respectively. Prior to initiation of the carburization, the reactor was heated to 500 ℃ and kept for 1 h to remove the crystal water in yellow H_2WO_4. Then after the reactor was heated again up to 700~750 ℃, the H_2WO_4 started to be reduced and carburized. In order to ensure completion of the solid-state reactions, the raw materials were soaked for 8~12 h at this temperature. After completion of the carburizing reaction, the quartz tube was removed from the reactor and quenched to normal temperature.

The as-prepared WC materials were characterized using X-ray diffraction and sorption analysis. A Rigaku DMAX-IIB diffractometer(CuK_α radiation, 1.540 5 Å) was used to determine the crystalline structures. The interplanar spacings d corresponding to the following sets of indices were accurately determined as (100), (101) and(110) for W_2C, and(001), (100) and(110) for WC. The molar fraction of WC or W_2C phase was calculated from the X-ray diffraction patterns as[11]

$$x_1=\frac{h_1}{h_1+h_2},\quad x_2=\frac{h_2}{h_1+h_2} \tag{1}$$

where h_1 and h_2 are the peak heights of the most intense reflections of WC (d = 1.88 Å) and W_2C (d= 2.28 Å), respectively; x_1 and x_2 are the molar fractions of WC and W_2C, respectively.

The surface area of the tungsten carbide samples was determined by BET test with low temperature nitrogen adsorption. The samples were degassed in vacuum, flowing He or flowing H_2 at 773 K for at least 1h before analysis. The average particle size was estimated using the following equation[12]:

$$d\rho=\frac{6}{\rho S_g} \tag{2}$$

where ρ is the bulk tungsten carbide density and S_g is the surface area determined by BET analysis. Use of this equation assumes that the particles were spherical or cubic.

The WC electrodes were prepared by cold pressing the mixtures of tungsten carbide particle and PTFE binder onto the metal mesh substrates. In this experiment, copper, lead and nickel mesh are used as substrates. Surface area of each electrode is 3 cm^2 and the loading of tungsten carbide particle is about 4 Pa for cathode and 40 Pa for anode respectively. The pressure for each electrode is about 10 MPa.

Using EG&G 273 electrochemical workstation the electrochemical properties was tested. Pt electrode (6 cm^2) was used as working electrode, SCE and Hg/HgO electrode were used as reference electrode in acid solution and alkaline solution, respectively. The test temperature was controlled within ±2 ℃.

3 RESULTS AND DISCUSSION

3.1 Crystal structure BET measurement

As reported previously[13], by controlling the initial raw materials and the reaction condition, the different tungsten carbide phases such as WC (HCP), W_2C (HCP) or WC_{1-x} (HCP) with different crystal structures can be obtained. Most of the authors quoted 750~850 ℃ carburization temperature and 2~6h duration time as the optimum conditions[14]. Some studies show that at temperature lower than 750 ℃ carburization is incomplete. A complete carburization during a synthesis carried out at 700 ℃ for 4h has been reported only by Ross[15]. Furthermore, the gaseous carburization agents have also influence on the final product. CH_4 is the most commonly used agent, and CO is a suitable agent for low temperature carburization[16]. In our experiment, we found that the crystal structure and phase components of the final tungsten carbide products can be modified by controlling the reaction conditions including reaction temperature, reduction gas flowing rate and duration time. Depending on XRD analysis, after reduction at 500 ℃ for 1 h, the yellow tungsten acid can almost be reduced to pure W. In the lower temperature and(or)

lower gas flow rates, e. g. 700 ℃, the major phase is W_2C(HCP) with a small amount of WC(HCP) and pure W metal coexisting in the as-prepared materials. For this sample, the calculated abundance of W_2C major phase is up to 71% according to Eqn. (1), and the residual phases are composed of W, free carbon and WC phase. The content of WC phase increases with the increase of reaction temperature and gas flowing rate. When the reduction temperature is up to 750 ℃, CO flowing rate up to about 480 mL/(h·g) H_2WO_4 and the duration time up to 12 h, the as-prepared materials are mainly composed of WC major phase(> 69%) and a small amount of W_2C phase and free carbon(without pure W metal coexistence).

The BET measurement shows that the surface area of the samples varies within a wide range from 4~ 5 m^2/g to 25~ 30 m^2/g depending on the prepared conditions. The values of surface area have closed relationship with the phase components of the samples. For the samples with major WC phase, the surface area is higher(25 ~ 30 m^2/g), and the surface area is only 5~ 10 m^2/g for the sample with major W_2C phase. According to the Eqn. (2), the average particle sizes are estimated to be in the range of several hundreds of nanometers. Considering the porous structure of the as-prepared materials, the real particle sizes may be in micrometer grade.

3.2 Electrochemical performances of W_2C cathode

Depending on the previous works, the tungsten carbide with different phase components shows different electrocatalytic properties, especially in different solutions. Nikolov et al [17] have disclosed that the electrocatalysts synthesized from white H_2WO_4 with major W_2C phase structure exhibit higher electrocatalytic properties for the hydrogen anodic oxidation reaction in concentrated H_3PO_4 solution. However the corrosion resistivity of W_2C derived from H_2WO_4 at elevated temperatures is very poor. At 150 ℃ and with current densities of 500 A/m^2, these electrodes displayed stable operation during the initial 200~ 220 h, then their polarization increased remarkably. For this reason, it is concluded that the tungsten carbide synthesized from white H_2WO_4 is not a suitable catalyst for the oxidation of hydrogen in phosphoric acid. But some studies disclosed that WC electrocatalysts synthesized from yellow H_2WO_4 show higher stability.

In this experiment, we used the yellow H_2WO_4 as initial raw material to synthesize the tungsten carbide electrocatalysts. At first, the materials with major W_2C phase were used as cathodic material, and its cathodic polarization properties in different solutions were measured using electrochemical methods. Figs. 2~ 5 illustrate the cathodic polarization curves in different solutions, and it is apparent that an obvious Tafel region existed for each curves. Fig. 2 shows the dependence of potential of W_2C electrode using Cu mesh as substrate on the current density in 20% NaOH electrolyte solution, and the electrode has been working in 20% NaOH electrolyte solution for 500 h with current density of 2 kA/m^2 at 323 K. As shown in Fig. 2, with the increase of current density and working temperature, the potential of electrode increased accordingly.

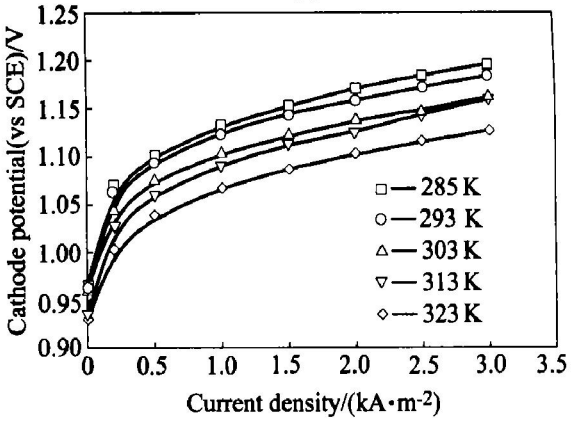

Fig. 2 Polarization curves of W_2C-PTFE-Cu electrode in 20%NaOH electrolyte solution (after 500 h electrolysis with current density of 2 kA/m^2 at 323 K)

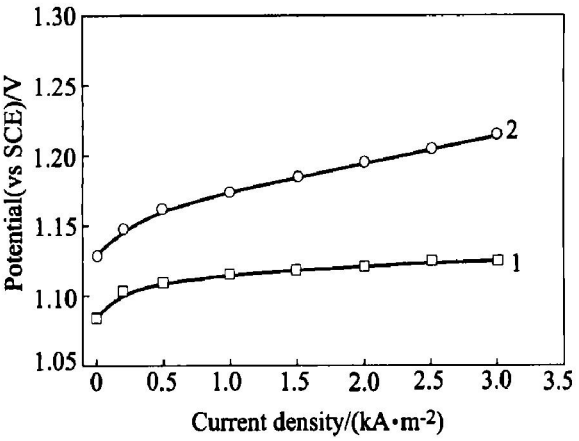

Fig. 3 Polarization curves of W_2C-PTFE-Pb electrode in H_2SO_4 solution at 298 K

1—4.95 mol/L H_2SO_4, 293 K, after 3 h electrolysis with current density of 2 kA/m^2 at 323 K, 2—300 g/L H_2SO_4+ 200 g/L $(NH_4)_2SO_4$, after 200 h electrolysis with current density of 2 kA/m^2 at 323 K

Fig. 3 shows the dependence of potential of W_2C-PTFE-Pb electrode on the current density in different solutions. Under the same electrolytic conditions, with the addition of $(NH_4)_2SO_4$, the polarization of W_2C-PTFE-Pb electrode became much higher than that in pure sulfuric acid solution. For example, at a current density of

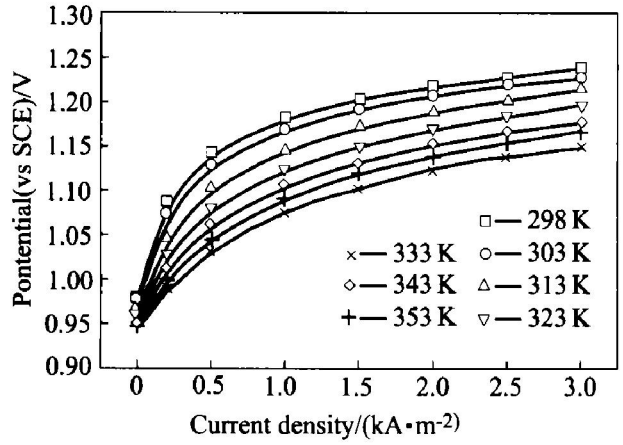

Fig. 4 Cathode polarization of W_2C-Ni electrode in 20% NaOH solution (after 24 h electrolysis with current density of 300 kA/m^2 at 323 K)

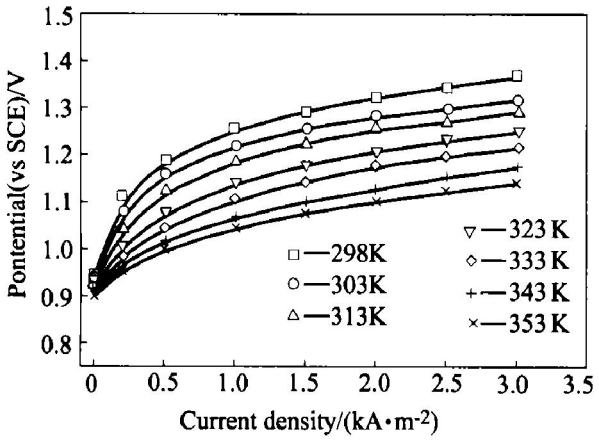

Fig. 5 Polarization curves of W_2C-Ni electrode in 120 g/L NaOH+ 160 g/L NaCl solution (after 24 h electrolysis with current density of 300 kA/m^2 at 323 K)

1 kA/m^2, the potential difference of the same electrode was up to 240 mV.

Furthermore, the cathodic performances of W_2C-Ni electrodes were performed in NaOH and NaOH+ NaCl solutions. As shown in Fig. 4 and Fig. 5, with the addition of NaCl, the electrode potential has a slight increase under the same polarization conditions. For example, at a current density of 1 kA/m^2 and 298 K, the potential difference was about 70 mV. By comparing Fig. 4 with Fig. 2, it was found that the overpotential of WC-Ni electrode was higher than WC-PTFE-Cu electrode in 20% NaOH solution under the same conditions. Due to the higher electrical conductivity of copper mesh, the electrode prepared onto copper mesh gives much higher conductivity than W_2C-Ni electrode does. It can be concluded that the ohmic potential drop of W_2C-Cu electrode is lower than that of W_2C-Ni electrode.

Depending on the polarization curves, the according kinetic parameters for W_2C hydrogen cathode in different solutions are calculated and presented in Table 1.

As shown in Table 1, W_2C electrodes exhibit the higher electrocatalytic properties like Pt electrodes. Under the same conditions, the same electrode gives the higher exchange current J_0 in alkaline solutions, which implies that the W_2C-type electrocatalysts are suitable to be used as hydrogen evolution electrodes and show potential applications in water electrocatalysis industry.

3.3 Electrochemical performances of WC anode in HCl solution

In this paper, the anodic properties of W_2C and WC electrodes in HCl solutions were also investigated. Fig. 6 depicts the anodic polarization curves of WC and W_2C electrodes in 12% HCl solution. As shown in Fig. 6, the overpotential of the two-type electrodes all increased as the current density increased. The overpotential of WC electrode is much lower than that of W_2C electrode at the same current density. The potential difference between these two electrodes was the largest at the current density of 100~ 300 A/m^2. When the current density is more than 400 A/m^2, the potential difference decreases up to 100 mV. The results show that the WC-type electrode exhibits higher electrocatalytic property for hydrogen anodic oxidation than that of W_2C-type electrode.

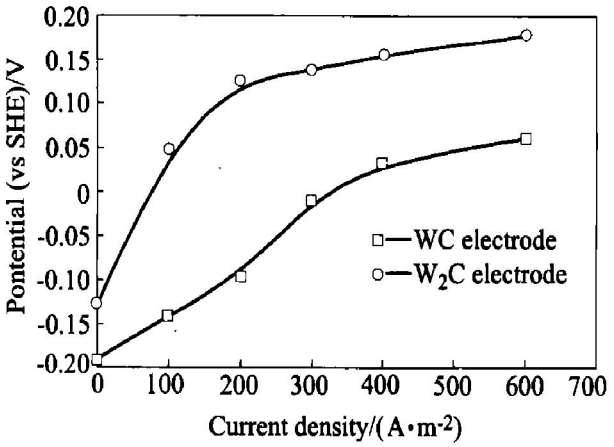

Fig. 6 Anodic polarization curves of WC and W_2C electrodes in 12% HCl solution

According to the above curves, the kinetic parameters of WC anode for hydrogen anodic oxidation reaction were calculated and presented, as listed in Table 2. The Tafel slope of WC electrode is two times as large as that of W_2C electrode, indicating the different mechanism of hydrogen anodic oxidation for the two electrodes. The WC electrodes show the similar electrocatalytic properties as Pt electrode depending on the exchange current density J_0. However, W_2C electrode exhibits the poor electrocatalytic properties, and its exchange current density is hundreds of times as low as that of WC electrode. For the hydrogen anodic oxidation in HCl solutions, WC electrode is apparently a suitable electrocatalyst.

Table 1 Kinetic parameters of W_2C electrodes for hydrogen evolution (Tafel equation: $\eta = a + b\lg J$)

Electrode	Electrolyte	T/K	a	b	α	J_0/(A·cm^{-2})
W_2C-PTFE-Cu	20% NaOH	293	0.272	0.103	0.567	2.24×10^{-3}
		313	0.245	0.09	0.687	2.95×10^{-3}
W_2C-PTFE-Pb	4.95 mol/L H_2SO_4	353	0.198	0.08	0.916	2.59×10^{-3}
W_2C-PTFE-Pb	300 g/L H_2SO_4+ 200 g/L $(NH_4)_2SO_4$	293	0.423	0.219	0.266	1.19×10^{-3}
W_2C-Ni	20% NaOH	298	0.327	0.125	0.472	2.42×10^{-3}
		313	0.325	0.142	0.440	5.11×10^{-3}
		353	0.253	0.121	0.579	7.97×10^{-3}
W_2C-Ni	120 g/L NaOH+ 160 g/L NaCl	298	0.528	0.216	0.274	3.52×10^{-3}
		313	0.473	0.214	0.290	6.15×10^{-3}
		353	0.270	0.128	0.547	7.70×10^{-3}

Table 2 Kinetic parameters for WC and W_2C electrodes for hydrogen anodic oxidation (Tafel equation: $\eta = a + b\lg J$)

Electrode	Electrolyte	T/K	a	b	α	J_0/(A·cm^{-2})
WC-PTFE	12% HCl	313	0.546	0.258	0.76	7.63×10^{-3}
	22% HCl		0.515	0.249	0.75	8.58×10^{-3}
	28% HCl		0.521	0.247	0.75	7.74×10^{-3}
	31% HCl		0.529	0.244	0.75	6.81×10^{-3}
W_2C-PTFE	12% HCl	313	0.516	0.116	0.46	3.42×10^{-5}

[REFERENCES]

[1] Böhm H. New non-noble metal anode catalysts for acid fuel cells[J]. Nature, 1970, 227: 484 - 485.

[2] Levy R, Boudart M. Platinum-like behavior of tungsten carbide in surface catalysis[J]. Science, 1973, 181: 547 - 548.

[3] Böhm H. Fuel cell assemblies with an acidic electrolyte [J]. J Power Sources, 1976,1: 177 - 192.

[4] Bodoardo S, Maja M, Penazzi N, et al. Oxidation of hydrogen on WC at low temperature[J]. Electrochimica Acta, 1997, 17: 2603 - 2609.

[5] Burstein G T, Barnett C J, Kucernak A R J, et al. Anodic oxidation of methanol using a new base electrocatalyst[J]. J Electrochemistry Soc, 1996, 143(7): 189 - 190.

[6] Iglesia E, Ribeiro F H, Boudart M, et al. Synthesis, characterization and catalytic properties of clean and oxygen-modified tungsten carbides[J]. Catalysis Today, 1992, 15: 307 - 310.

[7] Lee J S, Yeom M H, Lee D S. Catalysis by molybdenum carbide in activation of carbon-carbon, carbon-oxygen and carbon-hydrogen bonds[J]. J Mol Catal, 1990, 62: 45 - 49.

[8] Costa P D, Lemberton J L, Potvin C, et al. Tetralin hydrogenation catalyzed by Mo_2C/Al_2O_3 and WC/Al_2O_3 in the presence of H_2S[J]. Catalysis Today, 2001, 65: 195 - 200.

[9] Barnett C J, Burstein G T, Kucernak A R J, et al. Electrocatalytic activity of some carburised nickel, tungsten and molybdenum compounds[J]. Electrochimica Acta, 1997, 42(15): 2381 - 2388.

[10] Maas K P. H_2-O_2 fuel cell stacks with alkaline electrolyte [A]. Proceedings 28th Power Sources Symposium[C]. The Electrochemical Society Inc, Princeton, NJ, 1978. 35.

[11] Vidick B, Lemaitre J, Delmon B. Control of the catalytic activity of tungsten carbides-II physicochemical characterizations of tungsten carbides[J]. J Catalysis, 1986, 99: 428 - 438.

[12] Neylon M K, Choi S, Kwon H, et al. Catalytic properties of early transition metal nitrides and carbides: *n*-butane hydrogenolysis, dehydrogenation and isomerization [J]. Applied Catalysis A: 1999, 183: 253 - 263.

[13] Nikolov I, Nikolova V, Vitanov T. The preparation of the white tungstic acid modification and its use for the synthesis of highly active tungsten carbide[J]. J Power Sources, 1981/82, 7: 83 - 94.

[14] Fleischman R, Bohm H. Hydrogen oxidation on different tungsten carbide materials [J]. Electrochimica Acta, 1977, 22: 1123 - 1127.

[15] Ross P N, Stonehart P. The relation of surface structure to the electrocatalytic activity of tungsten carbide[J] . J Catal, 1977, 48: 42 - 47.

[16] Gao L, Kear B H. Low temperature carburization of high surface area tungsten powders[J]. Nanostructured Materials, 1995, 5(5): 555 - 569.

[17] Nikolov I, Vitanov T, Nikolova V. The effect of the method of preparation on the catalytic activity of Tungsten carbide for hydrogen evolution[J]. J Power Sources, 1980, 5: 197 - 206.

(Edited by YANG Bing)