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Study on hydrogen evolution performance of the carbon supported PtRu alloy film electrodes

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Abstract: The carbon supported PtRu alloy film electrodes having Pt about 0.10 mg/cm^2 or even less were prepared by ion beam sputtering method (IBSM). It was valued on the hydrogen analyse performance, the temperature influence factor and the stability by electroanalysis hydrogen analyse method. It was found that the carbon supported PtRu alloy film electrodes had higher hydrogen evolution performance and stability, such as the hydrogen evolution exchange current density (j^0) was increase as the temperature (T) rised, and it overrun 150 mA/cm^2 as the trough voltage in about 0.68V, and it only had about 2.8% decline in 500 h electrolytic process. The results demonstrated that the carbon supported PtRu alloy film electrodes kept highly catalytic activity and stability, and it were successfully used in pilot plant for producing H_2 on electrolysis of H_2S.

Key words: carbon supported PtRu alloy; film electrodes; hydrogen evolution performance

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1 Introduction

It is the key problem that how to transform efficiently electric energy into hydrogen energy for propel

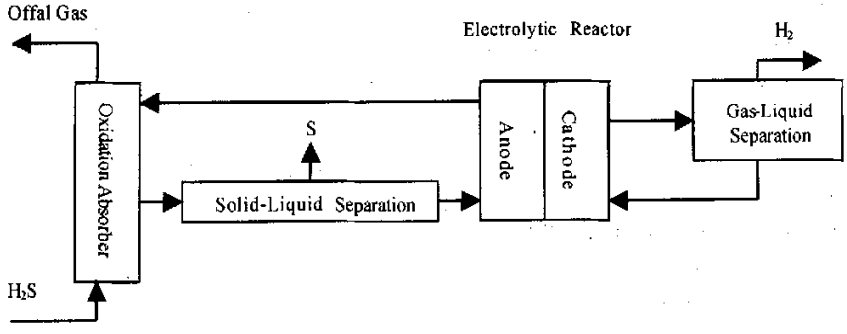

Fig.1 The flowchart of indirect electrolysis of H_2S

the clean energy use extensively[1]. At present, the advanced method could avoid passivation of anode by

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sulfur[2], and it only consumed 1/2-1/3 electricity than that by water electrolysis[3], its basic flowsheet was shown in Fig. 1.

Every kinds of hydride such as H_2S and so on[1-3], could be used to produce hydrogen by the way of electrolysis under fixed conditions from the view of theory. The processes in electrolysis can be divided into two different parts:

Electrolytic oxidation:

$$\text{Hydride} \xrightarrow{-ne} \text{Oxide} + nH^+ \tag{1}$$

Electrolytic reduction:

$$nH^+ \xrightarrow{+ne} \frac{n}{2}H_2 \tag{2}$$

It was found that platinum is one of the better catalytic electrode materials on hydrogen evolution[3]. Because of its expensive price, the cost to produce hydrogen by electrolysis would go up if the loaded Pt on the electrode is large. So it became the hot spot to cut down the consumption of Pt on electrode.

The three-phase reactions of gas-liquid-solid for preparation of hydrogen could be occurred upon the electrode surface by the tenet, and the metal of solid phase only play the role of conducting electron. At the same time, the front of electrode under the electric field would have the most powerful electric field intensity, and other indirect face to electrode had feebler powerful electric field intensity. When the single reaction happened on the electrode, the more powerful electric field intensity would make the more reactionary overpotential on corresponding place. It was known by the polarization equation (1) of electrode reaction:

$$I = I_0\left[\exp\frac{\Delta E}{\alpha n F} - \exp\frac{\Delta E}{\beta n F}\right] \tag{3}$$

where I is the macroscopic current on the electrode; ΔE is the over-potential of electrode reaction; I_0 is the reactionary current caused by positive and negative electrode at no macroscopic current passing through electrode; α and β are, respectively, reactionary transmit coefficient of positive electrode and negative electrode, respectively; n is the number of exchange electron of electrode reaction; F is constant of Faraday.

Because the catalytic material of thinner film on the electrode surface only had catalytic hydrolytic action, so other low-priced conducting materials could be used in transmit electron. On the same time, when the spread of gas had no great influence on the course of the electrode, the electrode of highly porosity structure would not make greater effect for reducing level of polarization of electrode surface. And at present, the electrolytic reaction mainly took place on the out of electrode surface. The above-mentioned principles had lay a theory foundation of film catalytic electrode application in the course of electrochemistry.

2 Experimentation and study

2.1 Manufacture of PtRu/C film electrodes by ISBM

The graphite cloths were used as substrates, the PtRu/C film electrode were manufactured by ISBM after cleaned by ultrasonic and by high-energy bombardment under high vacuum. The conditions of sputtering were shown in Table 1.

Table 1 The preparation conditions

Vacuum/Pa	Gas	Speedup Voltage/V	Bind Voltage/kV	Bind Current/mA
10^{-3}	Ar	−200	3.0-3.3	125-155

2.2 The performances of PtRu/C film electrode

The performances and result in temperature of PtRu/C electrodes were tested in the two-electrode electrolyzer and by the electrochemistry workstation. The conditions of testing were shown in Table 2.

The Hydrogen evolution working life and Pt content of PtRu/C electrodes were tested continuously in 500 h. The conditions of testing were shown in Table 3.

Table 2 The testing conditions of hydrogen analyse performance

Anode	4M H_2SO_4 +0.7M $FeSO_4$; The graphite cloths(25.5 cm^2)
Cathode	4M H_2SO_4; The carbon supported PtRu alloy film(0.95 cm^2)
Dissepiment(Nafion 117#); Space between(10mm); Voltage(1*,2*,3*); Temperature(1*,2*,3*); Instrument (CHI 650A)	

Note: 1* (20℃); 2* (1.4V, 20℃); 3* (20-60℃).

Table 3 The testing conditions of hydrogen analyse life-span

Anode	2M H_2SO_4 +0.7M $FeSO_4$; The graphite cloths(158.24 cm^2)
Cathode	2M H_2SO_4; The carbon supported PtRu alloy film(158.24 cm^2)
Velocity of flow of reaction liquid(250 L/h); Dissepiment(Nafion 117#); Voltage (1.6V); Temperature(20-40℃); Time(500 h); Instrument(HYL-A model)	

3 Results and discussions

3.1 The hydrogen evolution properties of PtRu/C film electrodes under the linearity scan

The hydrogen evolution properties for nine kinds of the carbon supported PtRu alloy film electrodes were shown in Fig.2. In this test, the electrolytic cell had not been adjusted because the different electrolytic cell would not affect j^0 and the trough voltage, the results would not image completely the best performance of the carbon supported PtRu alloy film electrodes, but it had no influence on comparatively comparing of performance. Fig.2 shows that No.1# and No.3# had better performance by assessed synthetically.

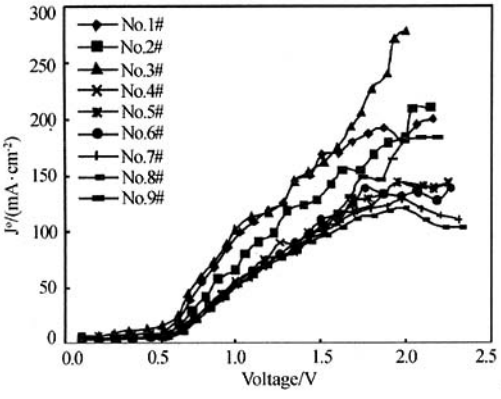

Fig. 2 The hydrogen analyse performance (20℃)

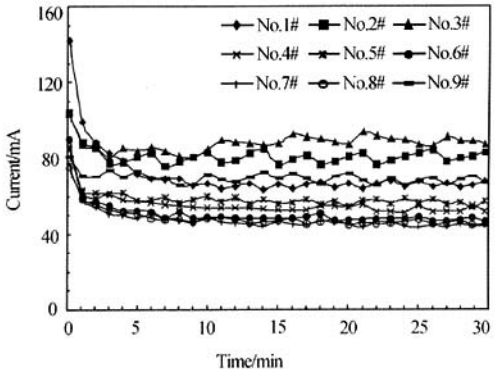

Fig.3 The hydrogen analyse performance (1.4 V, 20℃)

3.2 The hydrogen analyse performance of PtRu/C film electrodes in the constant voltage

The results of performance for nine kinds of the carbon supported PtRu alloy film electrodes were

shown in Fig.3. As a result of the hydrogen analyse performance in PtRu/C film electrodes, No.3# had synthetically higher hydrogen analyse performance and stability.

3.3 The performances of No.3# result in temperature

In this test, the electrolytic cell had been optimized for the sake of true performances, j^0 increased around 128% along with the temperature (T) changed from 20℃ to 60℃(See Fig.4). On account of high reacting temperature, the reaction rate and the difusion coefficient of reaction ion had increased also, and the agglutination degree of liquid had reduced. At the same time, the air bubble from liquid would affect testing results as temperature exceed 60℃, so we could not acquire directly steady data. But it would acquire linearity equation of j^0 and T that the data in temperature (20-60℃) by the "ARRHENIUS" equation, the comparative error of forecast value and practicality in temperature (20-60℃) all less than 2%.

$$\ln k_1/k_2 = E_a(T_2 - T_1)/RT_2T_1 \quad (4)$$

where k_1 and k_2 are reacting speed in different T, constant; E_a is reactied activation energy; T_1 and T_2 are reacting temperature.

We could acquire predicted value in temperature (60—90℃), and it showed that j^0 of No.3# had obtained 150 mA/cm² as the trough voltage in about 0.68 V and T in 70.7℃(See also Table 4 and Fig.5).

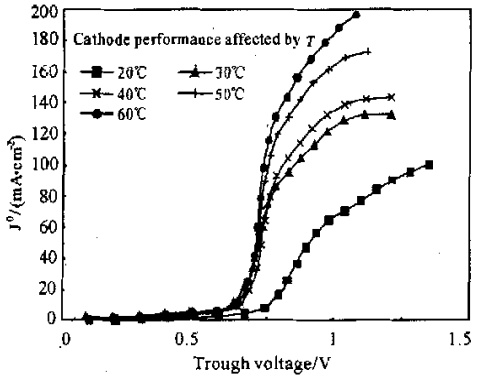

Fig.4 The hydrogen analyse performance (20—60℃)

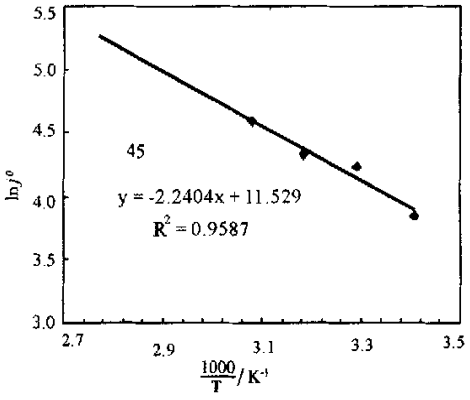

Fig.5 The relationship between j^0 and T (20—60℃)

Table 4 The actual value and predicted one of j^0 in different temperature

	Experiment				Forecast	
T/℃	Voltage/V	ln j^0	j^0/(mA·cm^{-2})	(1000×T/K)$^{-1}$	ln j^0	j^0/(mA·cm^{-2})
20.0	0.743	3.84	46.64	3.411	3.89	48.74
30.0	0.656	4.23	68.67	3.299	4.22	67.71
40.0	0.686	4.36	78.04	3.193	4.37	79.41
50.0	0.684	4.59	98.95	3.095	4.60	99.09
60.0	0.684	4.78	119.66	3.002	4.80	122.01
70.0	—	—	—	2.914	5.00	148.42
70.7	—	—	—	2.907	5.01	150.00
80.0	—	—	—	2.832	5.18	178.57
90.0	—	—	—	2.754	5.36	212.65

3.4 Hydrogen evolution working life and Pt loss of No.3# electrodes

It was found that the No.3# electrodes possess stable H_2 evolution activity under the condition of cur-

rent density over 44.23 mA/cm^2. After 500 h working the hydrogen evolution performance decrease only about 2.8%(See Fig.6), it shows that the carbon supported PtRu alloy film electrodes kept highly catalytic activity and stability.

The Pt content of No.3# electrodes (0.067 mg/cm^2) was very less than it manufactured by CVD (> 1.0 mg/cm^2)[4], and also less than it manufactured by Silk Screen Printing and Plasm Jet Printing in laboratory[2], moreover, the ullage rate of Pt was lower than it on Pt/C film electrodes having used in pilot plant for producting H_2 by electrolysis of H_2S (about 10%)[3](See Table 5).

Table 5 The testing result of Pt content

Element	The PtRu/C film electrodes(500 h)		
	Start/(mg·cm^{-2})	End/(mg·cm^{-2})	Ullage rate/%
Pt	0.067	0.063	5.9

On the side, the ullage rate of Pt was not consistent with the hydrogen evolution performance decrease, it could only estimate: (1) On account of, the film belong to metastable state, under effect of electric field and temperature together, the electrochemistry area of film electrodes was reduced because that Pt particle on surface had moved and (or) aggregated result in change of crystallite granularity. (2) Because of loss of Pt particle on surface by electrolytic scouring. However, the particular reason in it will be further studied.

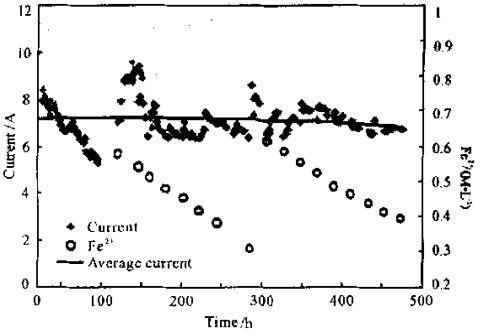

Fig.6 The testing of hydrogen analyse life-span

4 Conclusion

It was showed that the carbon supported PtRu alloy film electrodes made by IBSM method possess higher hydrogen evolution activity and stability, and it was successfully used in pilot plant for producing H_2 by electrolysis of H_2S. On the side, it was found that the carbon supported PtRu alloy film electrodes overrun 150 mA/ cm^2 as the trough voltage in about 0.68 V and T in 70.7℃. After 500 h electroanalysis, the hydrogen evolution activity only had about 2.8% decline, and the ullage rate of Pt only was 5.9%.

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