

THE EFFECT OF THE METHOD OF PREPARATION ON THE CATALYTIC ACTIVITY OF TUNGSTEN CARBIDE FOR HYDROGEN EVOLUTION

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Summary

The catalytic activity of tungsten carbide for the evolution of hydrogen in acid medium has been investigated. Specific activities were compared by taking current density values at a given potential in the straight line portion of Tafel curves. The real surface area of the electrodes was determined from capacitance measurements. It was shown that, depending on the starting material used, the activity of the carbides varied by a factor of up to three times. A relation was observed between catalyst activity and the average values of the Tafel slope. Thus, the results obtained confirm the assumption previously made that the different catalytic activity of tungsten carbides prepared from various starting materials for the anodic reaction is due to the different adsorption behaviour of the surface.

Introduction

Since the catalytic activity of tungsten carbide for hydrogen oxidation in acid solutions was determined [1] several papers have been published on the kinetics of the process [2 - 4]. A number of scientists have shown interest in the mechanism of the reverse reaction — evolution of hydrogen, because its clarification is important for the determination of the influence of the nature of the catalyst on the anodic reaction rate.

These investigations were performed on smooth tungsten carbide electrodes [2, 5 - 7]. Results show that this catalyst has a good activity for hydrogen evolution also. To date there are no data on the effect of the method of preparation of tungsten carbide on the rate of this process. In a previous paper [8] we showed that the catalytic activity of this catalyst for hydrogen oxidation depends on the type of starting material and does not depend on the carburization atmosphere. The aim of the present investigation was to determine whether the variation of these two parameters during the synthesis of

tungsten carbide affects its activity for hydrogen evolution and the kinetics of this process. The results obtained could clarify the relations determined for hydrogen oxidation on the same catalyst. The investigation was carried out on electrodes consisting only of the powder catalyst and PTFE so that any possible effect due to masking of the individual properties of the catalyst, prepared under different conditions, could be avoided.

Experimental

Preparation of tungsten carbide

A total of 30 samples was prepared as described in ref. 8 — reduction of the starting material in a hydrogen atmosphere, followed by carburization at 750 °C. The same starting materials (WO_3 , W_4O_{11} , W, $\text{H}_2\text{WO}_4(\text{yellow})$, $\text{H}_2\text{WO}_4(\text{white})$) and carburization atmospheres (CO ; $\text{CO} + \text{H}_2$; $\text{CO} + \text{Ar}$) were used. The BET surface areas were determined by adsorption of nitrogen (Table 1).

TABLE 1

Surface area (BET) measurements of starting materials and subsequent carbides

Starting material	Surface area (m^2/g)	
	Material	Carbide
W	3.4	3 - 3.8
W_4O_{11}	28	11.3 - 13.4
WO_3	17.2	10.6 - 12
$\text{H}_2\text{WO}_4(\text{w})$	22	9.2 - 11
$\text{H}_2\text{WO}_4(\text{y})$	20	7.8 - 9.5

The composition of the products was monitored by x.r.d. and chemical analysis [8].

X-ray analysis showed that complete carburization had taken place and no traces of tungsten were present. Chemical analysis showed variations in the composition: the carbon bound in the carbide lattice varied from 3.7 to 5.07 (6.12 is the stoichiometric value) and the free carbon from 0.2 to 0.7%.

Preparation of electrodes

A mixture of 40 mg of tungsten carbide and 40 vol.% PTFE powder was pressed on tantalum netting in a matrix. The final electrodes had an area of 1 cm^2 and were 250 - 400 μm thick.

Activity measurements

Current-potential curves were measured in 1N H_2SO_4 (A.K. grade distilled water) at 20 °C and at a controlled potential using a potentiostat with

an ohmic drop compensator (OH405 Radelkis, Hungary). Runs in the range from 0 to -300 mV (S.H.E.) on a given electrode were repeated until full coincidence of two successive curves was obtained. Measurements on different electrodes from one and the same catalyst were reproducible to within 10 - 15%.

The current densities were referred to unit real surface area, determined electrochemically from the charging curves by the method described in ref. 8. The Pt-black surface area used for comparing the activities was electrochemically determined from the hydrogen chemisorption within the range $+0.4$ to 0 V [9].

The results were treated by the method of least squares using an IZOT 310 (Bulgaria) computer; correlation coefficients were also determined for straight line plots.

Adsorption measurements

The coverage of the electrode surface with hydrogen, θ_H , is estimated from the charging curves which are recorded in the cathodic region. It is defined by the ratio:

$$\frac{q - q_{d.l.}}{Q_H}$$

q is the quantity of electricity which is required to reach a certain potential, φ , $q_{d.l.}$ is the quantity of electricity which is required for charging the double layer to this potential, and Q_H is the quantity of electricity which is required for covering the carbide surface with a monolayer of adsorbed hydrogen.

The values of q and $q_{d.l.}$ are determined from the charging curves. The value of Q_H is calculated by assuming that upon covering the carbide with a monolayer of adsorbed hydrogen, one hydrogen atom is evolved for each W atom. Under this condition the value of Q_H is given by the product of the number of W atoms on the electrode surface and the electron charge. The number of W atoms per unit surface area is calculated on the basis of the X-ray analysis data, which show that all investigated carbides have a hexagonal body centred lattice (1.88×10^{15} at/cm²). The model used for calculation of Q_H is idealized so the values obtained can serve only as a qualitative assessment.

Results and discussion

A typical current-voltage curve for each of the samples investigated is shown in Fig. 1. As can be seen from the Figure, the curve has a straight portion within the region -20 to -150 mV. The average values of the slope in this region and its maximum deviation (Δb) are shown in Table 2 for each group of samples prepared from a given starting material.

It can be seen from the Table that the values are dependent on the type of starting material. The exchange current densities determined from the

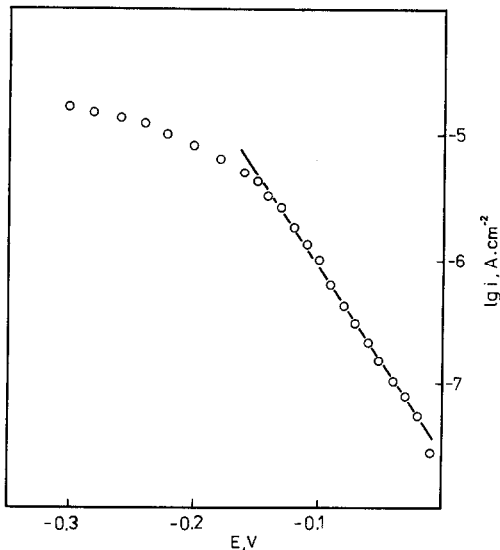


Fig. 1. Cathodic Tafel curve of a WC electrode in 1N H_2SO_4 ; $T = 20^\circ\text{C}$.

TABLE 2

Tafel slopes of tungsten carbides prepared from different starting materials

Starting material	Number of samples investigated	Number of measurements	b (mV)	Deviation Δb (mV)
W_4O_{11}	7	16	52.4	+6.6 -9.4
WO_3	5	11	52.3	+3.7 -6.3
$\text{H}_2\text{WO}_4(\text{w})$	7	13	58	+12 -8
W	5	10	67.2	+7.8 -11.2
$\text{H}_2\text{WO}_4(\text{y})$	6	12	76.2	+15.8 -12.2

Tafel region (-20 to -150 mV) vary between 0.02 and $0.05 \mu\text{A}/\text{cm}^2$ real surface. These values are in good agreement with the value found by Bohm [2] of $0.4 \mu\text{A}/\text{cm}^2$ geometric surface at 50°C , taking into consideration that current density increases about 3 times with a temperature change from 20 to 50°C , and the roughness coefficient for mechanically polished electrodes is 3 - 4. Our results are considerably lower than those of Palanker [6], $8 \mu\text{A}/\text{cm}^2$ geometric surface at 50°C . This might be due to the fact, that Palanker's electrodes were not polished and had a large roughness coefficient. The current density at 0.08 V was arbitrarily taken as a measure of catalyst activity. For a given set of electrodes a linear relationship is obtained between the current and the capacity (Fig. 2), but the difference in slope of these relationships shows that specific activity is dependent on catalyst history.

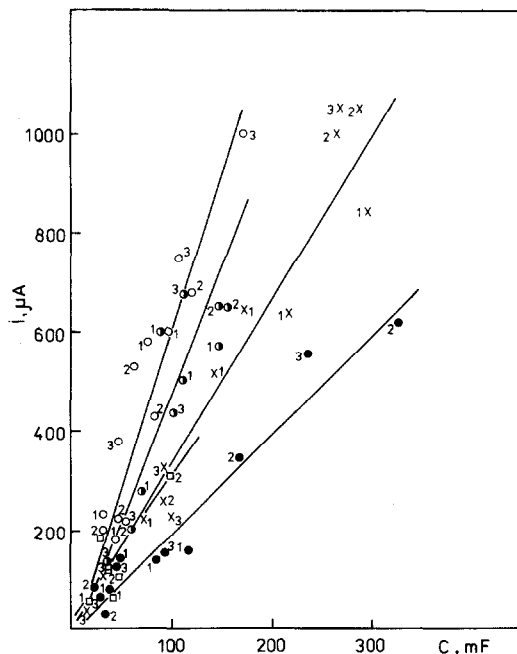


Fig. 2. Current-capacity plots of WC electrodes; starting materials: □ - W; ○ - W_4O_{11} ; ● - WO_3 ; X - H_2WO_4 (white); ● - H_2WO_4 (yellow); carburization atmospheres: 1 - CO; 2 - CO + H_2 ; 3 - CO + Ar. Correlation coefficients: □ - 0.84; ○ - 0.97; ● - 0.99; X - 0.97; ● - 0.94.

The carbides investigated can be classified into three groups: catalysts prepared from WO_3 and W_4O_{11} show best activity, less active are those prepared from H_2WO_4 (w) and W, and the least active those prepared from H_2WO_4 (y). On the other hand no relation is observed between the specific activity of carbides and the carburization atmosphere. This can be clearly seen in Fig. 2, where, for a given carbide starting material, data obtained from electrodes prepared from catalysts synthesised in different gas media lie on the same current-capacity plot. A comparison between these results and data obtained from the investigation of the reverse reaction, anodic oxidation of hydrogen, on these catalysts, shows that a similar relation exists between activity and the type of starting material, and activity is not dependent on carburization atmosphere [8].

No clear relation was established between the specific activity and the amount of carbon bound in the crystal lattice (Fig. 3), as was also found in the investigation of the anodic reaction [8].

When comparing the order of the change of activity (Fig. 2) with the average values of the Tafel slopes b (Table 1) the following dependence emerges: the b values decrease with increase of the catalytic activity.

To determine the rate controlling step of the process the correlations η/pH and i/pH were investigated in a mixed electrolyte with constant ionic strength (Figs. 4 and 5). Then the adsorbed hydrogen coverage θ_H (Table 3)

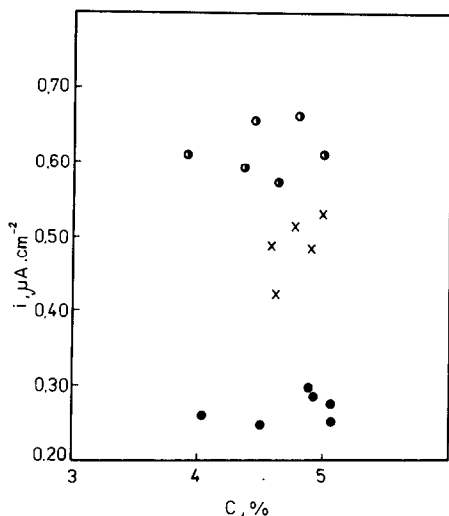


Fig. 3. Current density *vs.* carbon content in the crystal lattice. Starting materials: ○ - WO_3 ; X - $\text{H}_2\text{WO}_4(\text{w})$; ● - $\text{H}_2\text{WO}_4(\text{y})$.

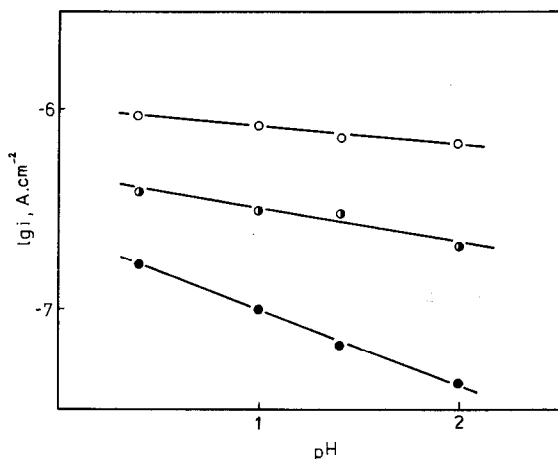


Fig. 4. $\lg i/\text{pH}$ dependence of WC electrodes; starting materials: ○ - W_4O_{11} ; ● - WO_3 ; ● - $\text{H}_2\text{WO}_4(\text{y})$. $\eta = -80$ mV.

was determined. From the Table it is seen, that even at low cathodic potentials (-10 to -30 mV), $\theta_{\text{H}} > 0.2$. This suggests that the hydrogen evolution reaction (h.e.r.) on these carbides occurs under Temkin conditions of adsorption [10]. The kinetic relationships for this case have been determined by Thomas [11] and Conway and Salomon [12]. Table 4 presents the experimental values of the kinetic parameters and those calculated by Conway [12]. The comparison shows that the experimental values coincide both with those calculated for the reaction atom + ion under activated adsorption and with

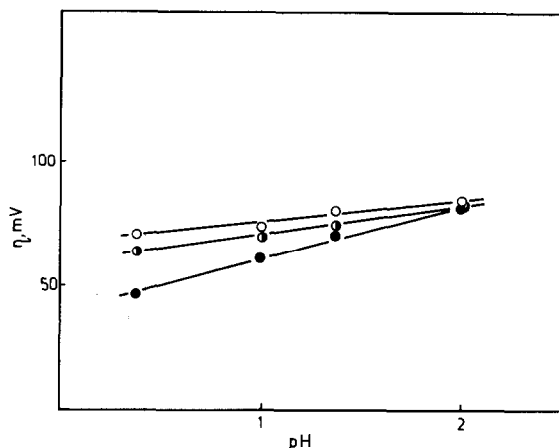


Fig. 5. η /pH dependence of WC electrodes; starting materials: ○ - W_4O_{11} ; ● - WO_3 ; ● - $H_2WO_4(y)$; $i = \text{const}$.

TABLE 3

Coverage of the electrode surface with adsorbed hydrogen (θ_H)

Carbides	θ_H at -10 mV (S.H.E.)	θ_H at -30 mV (S.H.E.)
WC(W_4O_{11})	0.48	0.60
WC(WO_3)	0.39	0.49
WC(H_2WO_4y)	0.23	0.30

those for neutralization of H_2^+ under activated adsorption conditions, provided that the values of β and γ^* vary. Further investigation is required to determine which of the two steps is rate determining. The possibility for variation of the β and γ values which is suggested by the experimental evidence, may be caused by the type of starting material, *i.e.*, there are areas of different adsorption energy for hydrogen on the surface of the tungsten carbide powders. Thus, the results obtained confirm the assumption made during the investigation of the anodic reaction [8], namely, that the different catalytic activities of tungsten carbide powders prepared from different starting materials are due to a difference in their adsorption properties. Most probably the observed relations are determined by the different surface properties of the catalysts: crystal habit of the particles and chemical composition (a difference in the bulk and surface composition).

As shown in ref. 8, the crystal habit of the carbide particles investigated is different, depending on the type of starting material. This may well be one of the reasons for the difference in adsorption energy, as is observed for ins-

*Symmetry factors defined in refs. 11 and 13; the possibility of their variation is discussed by Thomas [11].

TABLE 4
Comparison of experimental and theoretical reaction order and other derivatives for the h.e.r.

Derivative	Theoretical*				Experimental			
	Atom-atom conc. soln. Temkin	Atom-ion conc. soln. Temkin	H ₂ neutralization conc. soln. Temkin		WC(w ₄ O ₁₁)	WC(wO ₃)	WC(H ₂ WO ₃)	
	Act.	Non act.	Act.	Non act.				
Tafel slopes	$\frac{RT}{2\beta F} = 59 \text{ mV}$	$\frac{RT}{2F} = 29 \text{ mV}$	$\frac{RT}{(\gamma + \beta)F} = 59 \text{ mV}$	$\frac{RT}{(1 + \beta)F} = 39 \text{ mV}$	$\frac{RT}{(1 + \beta)F} = 39 \text{ mV}$	48 mV	55 mV	78 mV
$\left(\frac{\partial \eta}{\partial \ln C_{H_3O^+}}\right)_{i\psi_1}$	0	0	$\frac{(1 - \beta)RT}{(\gamma + \beta)F} = 29 \text{ mV}$	$\frac{(1 - \beta)RT}{(1 + \beta)F} = 20 \text{ mV}$	$\frac{(\gamma - \beta)RT}{(\gamma + \beta)F} = 0$	8 mV	11 mV	23 mV
$\left(\frac{\partial i}{\partial \ln C_{H_3O^+}}\right)_{\eta\psi_1}$	0	0	$(1 - \beta) = 0.5$	$(1 - \beta) = 0.5$	$(\gamma - \beta) = 0$	0.14	0.20	0.37

*Taking $\beta = 0.5$ and $\gamma = 0.5$

tance with the adsorption of H_2 , O_2 , etc., on different Pt single-crystal surfaces in gas and liquid media [14, 15].

The same effect may be expected as a result of the different chemical composition of the surface layers. This is the finding of Bohm [16] when investigating the process on smooth electrodes. Obviously further investigations are necessary to determine which of the two surface properties of carbides plays the predominant role in the determination of the catalytic activity for the hydrogen reaction.

From the practical viewpoint, the current densities for hydrogen evolution that can be obtained from electrodes prepared from tungsten carbide powder may be of interest. Armstrong and Bell have made such an estimation for the activity of smooth electrodes [7]. Figure 6 shows current-voltage curves at $80^\circ C$ in $9.9N H_2SO_4$ on Pt-black electrodes ($3 mg Pt/cm^2$) and on electrodes which were prepared by us containing $40 mg/cm^2$ of tungsten carbide. It is seen that the current on the tungsten carbide electrode at $E = -100 mV$ is 10 times less than that on Pt-black electrodes. However, considering the lower price of tungsten carbide and the current densities obtained ($50 mA/cm^2$ at $E = -100 mV$ and $110 mA/cm^2$ at $E = -200 mV$) it can be considered as a useful catalyst for water electrolysis.

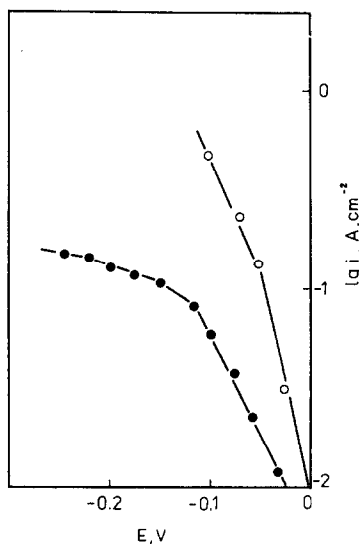


Fig. 6. Cathodic Tafel curves of a: ● - WC electrode ($40 mg/cm^2$) and ○ - Pt/Pt ($3 mg Pt/cm^2$) in $9.9N H_2SO_4$; $T = 80^\circ C$.

Conclusion

The activity of tungsten carbide for hydrogen evolution depends on the starting material. Tungsten oxides yield, under the same conditions of synthe-

sis, more active catalysts than tungstic acid or tungsten powder. The different catalytic activity of the investigated tungsten carbides is due to the different degree of adsorption of hydrogen. Tungsten carbides have good catalytic activity for hydrogen evolution and might be used for water electrolysis.

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