

THE EFFECT OF METHOD OF PREPARATION ON THE CATALYTIC ACTIVITY OF TUNGSTEN CARBIDE

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Summary

The catalytic activity of tungsten carbide for the oxidation of hydrogen in an acid medium has been investigated on sedimented powder electrodes. 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 employed, the activity of the carbides varied by half an order of magnitude. This observation is discussed in terms of differences in surface properties. No effect on activity was observed when changing the carburization atmosphere from carbon monoxide to a mixture of carbon monoxide and hydrogen or argon.

Introduction

Since the discovery of the catalytic activity of tungsten carbide for hydrogen ionization in acid solutions [1], many papers dealing with the optimization of this catalyst, and electrodes based on it, have been published. Although tungsten carbide is less active than platinum metal it has an important advantage — a unique ability to resist very strong catalytic poisons such as carbon monoxide, hydrocarbons, and hydrogen sulphide.

Recently, tungsten carbide electrodes, prepared by various methods, have been investigated [2 - 4] for their catalytic activity towards hydrogen oxidation in acid solutions. Although the activity is a very sensitive function of the method of preparation, no definite relation has been established between activity and the type of material from which the electrodes were prepared. Thus, whereas, Svata and Zabransky [2], and Ross and Stonehart [3] (investigating tungsten carbide gas diffusion electrodes) found a difference

in activity between carbides prepared from the amorphous white, and the crystalline yellow, modifications of tungstic acid, Palanker *et al.* concluded [4], from studies on carbides prepared from tungstic acid and tungsten powder, that activity was independent of the starting material and was a function of the surface area only. In addition, the effect on activity of different carburization media has not been established, despite several studies using mixtures involving hydrogen [5 - 7], carbon dioxide [7], argon [6] or methane [8] as alternatives to pure carbon monoxide. In all these reports, the activity is referred either to the geometrical surface area of the electrode or to the true surface area determined by nitrogen adsorption (BET). In the former method, the activity data could contain many side effects (surface, structure, morphology), in the latter, the approach assumes that the electrode surface taking part in the adsorption of nitrogen is identical with that active in the electrochemical process. If PTFE or another binding agent is used in the manufacture of the electrodes [2, 3] part of the catalyst may be blocked; if no binding agent is employed, but large quantities of the catalyst are used (40 mg/cm^2) [4], screening of the particles can occur and lower the utilization of the active electrode materials. Such effects may explain the reported differences in electrode activity.

Further, no quantitative measurements of mass transport limitation were made in any of the published results on gas diffusion electrodes. This is also the case in a subsequent paper [9] concerned with the determination of tungsten carbide activity as a powder. The current-voltage curves obtained on the sedimented electrode employed in this work show diffusion limiting behaviour.

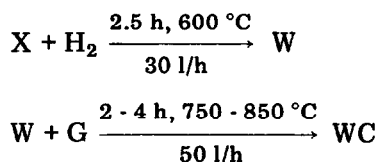
The electrodes employed by Sadkowski *et al.* [10] consisted of small amounts (up to 3.2 mg/cm^2) of tungsten carbide powder, mixed with PTFE emulsion, deposited on discs of hydrophobic carbon black. The discs were prepared similarly to the gas supplying layer of carbon-air electrodes [11]. In this case quantitative measurements of mass transport limitation were made but current densities were referred to surface areas of tungsten carbide determined by BET measurements.

The present paper is therefore aimed at obtaining reliable measurements of the specific activity of tungsten carbide electrodes so that the influence of starting materials and carburization media may be examined unambiguously.

Experimental

Tungsten carbide preparation

A total of 42 samples was prepared from four different raw materials. Catalysts from a given starting material were prepared using various experimental conditions and different carburization atmospheres. Carbide synthesis may generally be described by the equation:



where X is the starting material and G represents the gas or gas mixture under which carburization took place. The starting materials used were: (i) tungsten powder HC 40 and tungsten trioxide HC 525 (H. Starck, F.R.G.); (ii) yellow tungstic acid (VEB Hartmetallwerke Immelborn Roswein, G.D.R.); (iii) a white modification of tungstic acid prepared by a procedure described by Kulčický and Petrdlik [12]; (iv) blue oxides of tungsten (W_4O_{11}) obtained from the Technical University, Košice (Czechoslovakia). All chemicals were of 99% purity, the remaining 1% consisting in all cases of MoO_3 , Fe_2O_3 , SiO_2 , and CaO . The surface areas of the starting materials were between 3 and $28 \text{ m}^2/\text{g}$. The BET surface areas were determined by adsorption of nitrogen (Table 1). Pure carbon monoxide, and mixtures with hydrogen or argon as reducing and inert carriers, respectively, were employed. Hydrogen was produced by electrolysis and carbon monoxide and argon were of spectral purity.

The composition of the products was monitored by x.r.d. and chemical analysis. The total carbon contents of the carbides were determined by the amount of CO_2 evolved on combustion, and the free carbon contents were determined from the weight of carbon obtained after dissolution of tungsten carbide in acid solution.

X-ray analyses showed that complete carburization had taken place and no traces of tungsten were present. Chemical analyses showed variations in the composition: the carbon bound in the carbide lattice varied from 3.7 to 6.1 (full stoichiometry) and the free carbon from 0.2 to 0.9%. S.e.m. photographs were obtained using a JEOL type SEM-100B electron microscope. The orientation of the crystals after sedimentation of the carbide on the tantalum collector was examined by conventional X-ray texture goniometric

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	8 - 15.5
WO_3	17.2	3 - 13.4
H_2WO_4 (white)	22	5.5 - 15.7
H_2WO_4 (yellow)	25	3.7 - 11.8

analysis using a Müller-Mikro 111 diffraction equipment, with Co K_{α} radiation at $\theta = 21^{\circ}$.

Electrode preparation

Tungsten carbide (10 mg) was deposited for 10 h on a 7 mm dia. tantalum collector from 10 ml of an ethanol suspension. The catalyst loading was 1 mg which made an electrode 100 - 200 μm thick. After drying, the electrode was placed on a fritted glass disc which formed the bottom of a glass holder. At the commencement of an experiment, hydrogen was passed through a tube to purge air from the holder, and after 15 min the electrolyte was added to the electrochemical cell. A three-phase boundary was formed and maintained within the powder layer.

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 (OH 405 Radelkis, Hungary). Runs in the range from 0 to +350 mV (S.H.E.) on a given electrode were repeated until full coincidence of two successive curves was obtained. Different electrode measurements from one and the same catalyst were reproducible to within 10 - 15%.

In order to compare specific activities the current densities are referred to unit real surface area. This area was determined electrochemically and taken as the ratio of the double layer capacity of the working electrode to that of smooth tungsten carbide ($150 \mu\text{F}/\text{cm}^2$) [13]. The double layer capacity was calculated from charging curves (Fig. 1) which were recorded for each sample following the measurement of current-voltage curves (after the solution had been purged of hydrogen by bubbling through nitrogen for one hour) in the range +350 - +150 mV at a nitrogen pressure of 20 mm H_2O and for different charging currents (2, 4, 8 μA). For all currents used, a constant capacity value was obtained, showing that a quasi-equilibrium had been achieved. There was slight hysteresis between the anodic and cathodic branches of the curves (Fig. 1) but it did not exceed 10%.

Possible errors involved in the determination of the surface area by the capacity method described here include:

(i) the possible presence of carbon and/or tungsten oxides on the catalyst surface, which would increase the overall capacity, but would not take part in the electrochemical process;

(ii) an additional contribution to the charge passed from the reduction of oxides in the potential region under study.

To calculate the influence of free carbon, the charging curve for a pure carbon black electrode was determined and the double layer capacity calculated. A value of $6 \mu\text{F}/\text{cm}^2$ BET surface area was obtained (in agreement with the values reported in the literature [14]), and since <0.9% of free carbon was present in our samples, the error due to this effect is below 0.5%.

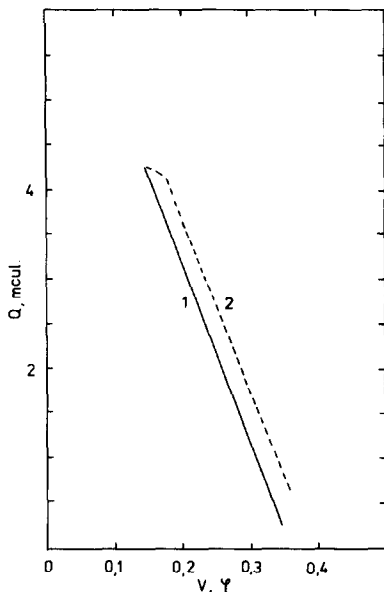


Fig. 1. Charging curve of a sedimented WC electrode in 1N H_2SO_4 ; $t = 20^\circ\text{C}$; $\Delta P_{\text{N}_2} = 20 \text{ mm H}_2\text{O}$. 1, cathodic branch; 2, anodic branch.

To estimate the influence of tungsten oxides on the double layer capacity, X-ray analyses of the samples were made after current-voltage measurements had been completed. Of a total of 42 samples, 4 contained oxides and were discarded.

The results were treated by the method of least squares using an IZOT 0310 (Bulgaria) computer; correlation coefficients were also determined for straight line plots.

Results and discussion

A typical current-voltage curve for each of the samples is shown in Fig. 2. The current density at 0.08 V was arbitrarily taken as a measure of catalyst activity. Exchange current densities were determined from the Tafel region (0 - 120 mV). The c.d., the e.c.d., and values of the average slope, together with the maximum deviation (Δb) for each group of samples prepared from a given starting material, are given in Table 2. From these values it can be seen that the catalytic activity is dependent on the choice of starting material. For a given set of electrodes a linear relationship is obtained between the current and the capacity (Fig. 3), and this partly confirms the finding by Palanker *et al.* [15] that the activity is a function of the development of the surface area. However, electrodes obtained from different sources show dif-

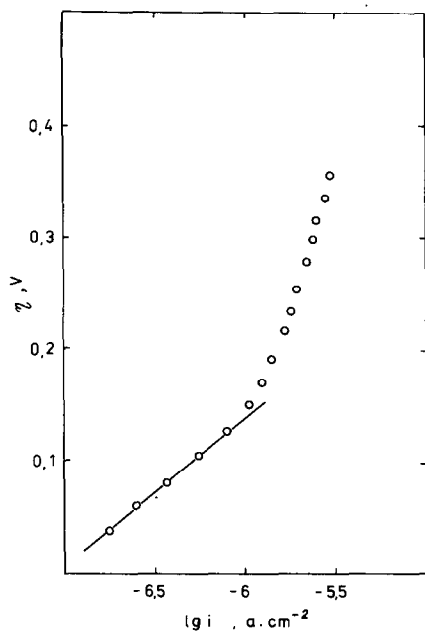


Fig. 2. Tafel curve of a sedimented WC electrode in 1N H₂SO₄; $t = 20^\circ\text{C}$; $\Delta P_{\text{H}_2} = 20 \text{ mm H}_2\text{O}$.

TABLE 2

Tafel slopes, exchange current densities (i_0) and current densities (i) at +80 mV (S.H.E.) of tungsten carbides prepared from different starting materials

Starting material	Number of samples investigated	b (mV)	Δb (mV)	$i_0 \times 10^8$ (A/cm ²)	$\Delta i_0 \times 10^8$ (A/cm ²)	$i \times 10^8$ (A/cm ²)	$\Delta i \times 10^8$ (A/cm ²)
W	7	111	-31	2.9	-0.6	11.4	-3
			+29		+1.6		+1.6
			-30		-0.7		-1.7
W ₄ O ₁₁	9	115	+35	3.9	+0.6	13.7	+2.1
			-26		-0.8		-1.4
			+16		+2.3		+2.9
WO ₃	7	126	-16	4.5	-0.4	15.1	-2.1
			+16		+0.5		+1.8
			-27		-0.6		-0.7
H ₂ WO ₄ (white)	8	124	+16	2.1	+0.5	6.5	+1.8
			-27		-0.6		-0.7
			+23		+0.5		+0.5
H ₂ WO ₄ (yellow)	7	97	+23	1.3	+0.5	2.2	+0.5

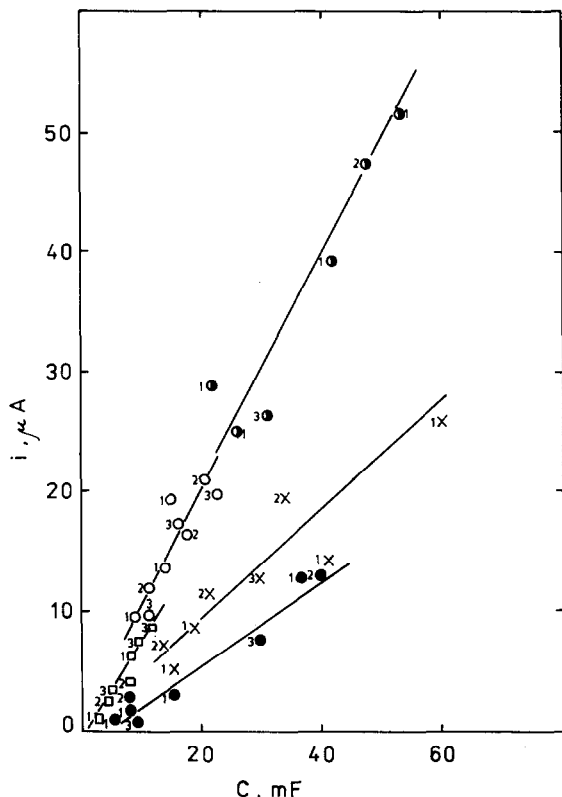


Fig. 3. Current-capacity plots for sedimented WC electrodes; starting materials: \square , W; \circ , W_4O_{11} ; \bullet , WO_3 ; \times , H_2WO_4 (white); \bullet , H_2WO_4 (yellow); carburization atmospheres: 1, CO; 2, CO + H_2 ; 3, CO + Ar. Correlation coefficients: \square , 0.97; \circ , 0.95; \bullet , 0.94; \times , 0.89; \bullet , 0.97.

The carbides investigated can be classified in two groups: samples prepared from tungsten oxides and samples synthesized from tungsten and tungstic acid. The activity of the former was half an order of magnitude higher than that of the latter. On the other hand, no relation was found between the activity of the catalyst and the carburization atmosphere used for formation. This can be clearly seen from Fig. 3 where, for a given carbide starting material, data obtained from electrodes prepared from catalysts synthesized in different gas media lie on the same plot of current-capacity. This is in contradiction to experimental results obtained by some other authors: for example, Hung *et al.* [5] obtained a more active catalyst on mixing carbon monoxide with hydrogen. The increased activity over electrodes prepared from pure CO was attributed to greater surface area. Similarly, Svata and Zabransky [6] found a higher activity in carbides prepared with hydrogen or argon as carbon monoxide carriers, but the authors offered no explanation for their findings. Ross *et al.* [16] attributed this effect to the reduction in partial pressure of CO, which results in a lower surface content of free carbon

on carbides prepared with a gas mixture than on those prepared with CO alone. With gas mixtures, the equilibrium in the disproportionation reaction of CO ($2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$) is shifted to the left-hand side, and the formation of carbon is slower. Thus, most of the carbon formed is consumed in the carburization process and there is little free carbon blocking the catalyst surface.

Free carbon does, however, accumulate on the surface of carbides prepared under CO alone (Table 3). But blocking effects are not reflected in our data since specific activities are referred to unit real surface area which is determined by an electrochemical method unaffected by the presence of the carbon (*v.s.*). Unlike previous work [5], surface area values showed no carburization atmosphere influence on the BET surface area (Table 4). This could be due to the different conditions used for syntheses; Hung *et al.* prepared their catalysts by a one-step process (reduction together with carburization), whereas the catalysts discussed here were reduced before carburization.

Finally, no clear relationship could be established between the activity and the amount of carbon bound in the crystal lattice (Fig. 4). Apart from one exception, all the catalysts were carbon deficient, which has been suggested [17, 18] as a criterion for good activity. However, no optimum carbon content was found.

We conclude that the differences in catalytic activities result from differences in surface properties such as particle morphology and the chemical composition of the surface layer, which may be significantly different from that of the bulk. S.e.m. analysis of samples of tungsten carbide from different sources showed significant differences in particle morphology (Fig. 5). This suggests that a preferential orientation of the powder particles may occur during deposition of the electrode. The texture goniometric analysis did not, however, substantiate this assumption.

TABLE 3

Influence of carburization atmosphere on the content of free carbon in three series of tungsten carbides. (Temperature and time of carburization are identical for each series.)

Starting material	Carburization atmosphere	Carbon content (%)
WO ₃	CO	0.85
	CO + Ar	0.57
	CO + H ₂	0.45
H ₂ WO ₄ (white)	CO	0.27
	CO + Ar	0.18
	CO + H ₂	0.13
H ₂ WO ₄ (yellow)	CO	0.90
	CO + Ar	0.67
	CO + H ₂	0.57

TABLE 4

Influence of carburization atmosphere on the surface area (BET) of tungsten carbides
(Temperature and time of carburization are identical for each series.)

Starting material	Carburization atmosphere	Surface area (m^2/g)
W	CO + Ar	3.4, 3.-
	CO + H ₂	4.9
	CO	3.6, 3.5
WO ₃	CO	6.8
	CO + Ar	6.1
W ₄ O ₁₁	CO	10.2, 14.5
	CO + Ar	10.4, 11.7, 11.7
	CO + H ₂	10.2, 11.-
H ₂ WO ₄ (white)	CO	9.9, 10.3
	CO + H ₂	7.2, 5.8
H ₂ WO ₄ (yellow)	CO	11.2, 11.8
	CO + H ₂	10.5, 10.9

It is therefore concluded that particle morphology or crystal habit has a strong influence on the rate of adsorption, and, hence, on the electrochemical oxidation of hydrogen on these tungsten carbide catalysts [19 - 21]. A

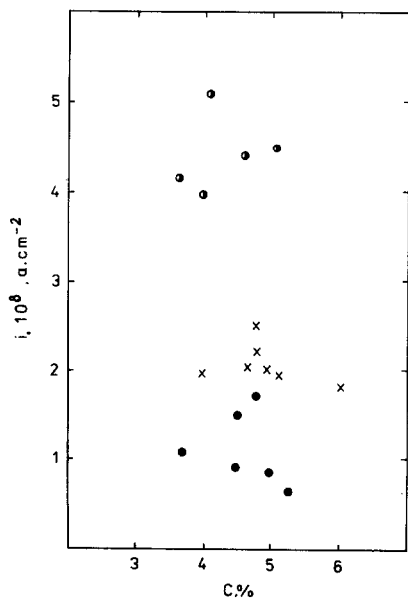
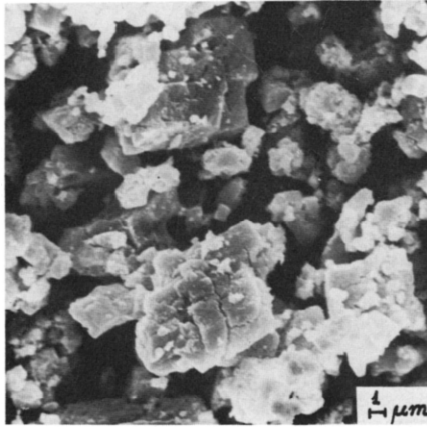
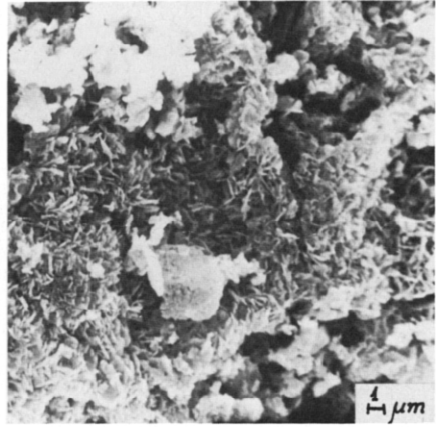


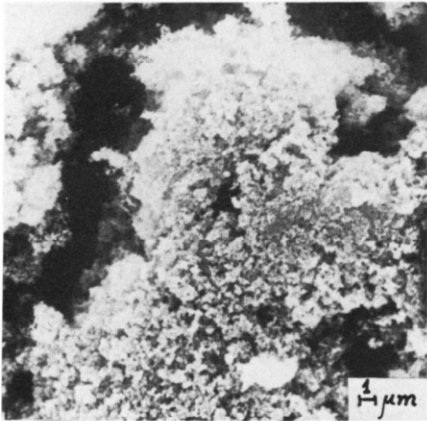
Fig. 4. Exchange current density *vs.* carbon content in the crystal lattice. Starting materials: \circ , WO₃; \times , H₂WO₄ (white); \bullet , H₂WO₄ (yellow).



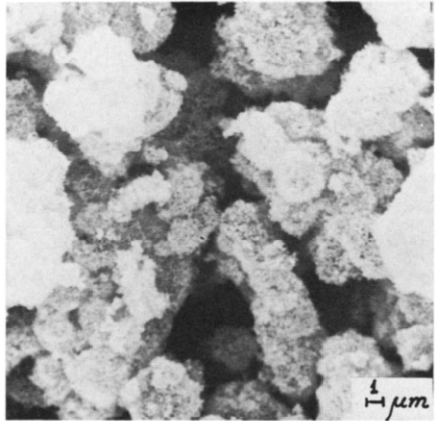
(a)



(b)



(c)



(d)

Fig. 5. S.e.m. photographs of tungsten carbide prepared from (a) H_2WO_4 (white); (b) WO_3 ; (c) W_4O_{11} ; (d) H_2WO_4 (yellow). Magnification: $\times 3\,000$.

similar effect can be expected resulting from the chemical composition of the surface layer, which can deviate considerably from that of the bulk phase [22]. Also, trace impurities may be involved in the process, but further investigations are required to establish the extent of their influence.

Conclusions

The activity of tungsten carbide for the oxidation of hydrogen depends on the starting material employed in the preparation of the catalyst. Tungsten oxides yield, under the same conditions of synthesis, more active catalysts than tungstic acid or tungsten powder.

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