

## THE PREPARATION OF THE WHITE TUNGSTIC ACID MODIFICATION AND ITS USE FOR THE SYNTHESIS OF HIGHLY ACTIVE TUNGSTEN CARBIDE

I. NIKOLOV, V. NIKOLOVA and T. VITANOV

*Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, 1040 Sofia (Bulgaria)*

(Received March 5, 1981)

### Summary

The conditions for the preparation of the white modification of tungstic acid are optimized by changing the basic parameters which control the specific surface. Samples with a highly developed surface ( $70 \text{ m}^2/\text{g}$ ) are obtained. It is shown that this property depends on the structure of the acid particles.

The acid samples were used for the synthesis of carbides with large surface areas ( $22 - 26 \text{ m}^2/\text{g}$ ), and high catalytic activity for the hydrogen evolution reaction in acidic media. The activity with regard to the anodic reaction of hydrogen is relatively less pronounced due to the poor corrosion resistance of these carbides.

---

### Introduction

The last decade has witnessed a keen interest by many research laboratories in the preparation and electrochemical behaviour of tungsten carbide. This was a result of the discovery by Bohm and Pohl [1] that tungsten carbide has a good catalytic activity for the hydrogen oxidation process in acidic media. Several patents and papers dealing with the conditions for the preparation of highly active tungsten carbides have been issued already [2 - 8]. Three of them [6 - 8] described the preparation of carbides from tungstic acid. Two [6, 8], are not aimed at the optimization of conditions to obtain a large surface area catalyst. They give data for the electrochemical activity for hydrogen oxidation of carbides synthesized from the white modification of tungstic acid, tungsten oxide, and tungsten [5], or the white and yellow modification of tungstic acid [8]. The experimental data presented point to the fact that carbides synthesized from the white modification of tungsten acid have a higher catalytic activity. The third report [7] is

concerned with the conditions for the preparation of highly dispersed tungstic acid ( $80 \text{ m}^2/\text{g}$ ) and its use for the synthesis of large surface area ( $30 \text{ m}^2/\text{g}$ ) carbides. This report does not specify which modification of tungstic acid was used in the syntheses, but considering the highly acidic solutions used for the precipitation of the acids ( $10 - 11 \text{ M HCl}$ ) and no preliminary alkalization of the  $\text{Na}_2\text{WO}_4$  solution, one can presume that it was the yellow tungstic acid modification [9].

The present paper is aimed at the determination of the conditions for the preparation of the highly dispersed white modification of tungstic acid and the synthesis of carbides with large specific surfaces since, according to refs. 8 and 10, the latter offer a higher catalytic activity than those obtained from the yellow modification.

## Experimental

### *Preparation of the white modification of tungstic acid*

Several methods for the preparation of the white modification of tungstic acid are given in the literature [11 - 13]. Depending on the pH value of the solution after the precipitating acid has been added, either the white (paratungstic), or the yellow (metatungstic) modifications of the acid are obtained. The former is stable up to  $\text{pH} = 4 - 5$  and the latter at  $\text{pH} = 2$  [9].

The use of tungstic acid as the initial material for the synthesis of highly active tungsten carbide required the preparation of the white modification of the acid with a large specific surface.

We prepared such a tungstic acid in the following way:  $\text{HCl}$  and  $\text{Na}_2\text{WO}_4 + \text{NH}_4\text{OH}$  ( $\text{pH} = 8 - 12$ ) solutions were cooled, and the  $\text{HCl}$  solution was slowly added to the alkaline solution with continuous stirring. During this operation the pH value of the solution slowly changes to approximately 6; further additions of small quantities of acid cause abrupt alterations of pH values. If we stop the addition of acid at  $\text{pH} = 4$ , a white suspension is obtained from which precipitation of the acid is very difficult and the yield is negligible. Therefore the following procedure is applied: after reaching  $\text{pH} = 5 - 6$ , the remaining  $\text{HCl}$  solution is quickly added and the pH of the solution attains values of  $1 - 2$ , forming a bulky precipitate. In order to prevent transition of the white modification into yellow, we must quickly decant the solution from the precipitate and replace it with distilled water. After several washings with distilled water until negligible amounts of chloride and ammonium ions are present, the tungstic acid precipitate is centrifuged, dried at  $70^\circ\text{C}$ , ground in a mortar, and used for the synthesis of tungsten carbide.

Over 80 experimental runs were carried out by changing the basic parameters which control the surface of the acid obtained:  $\text{HCl}$  concentration;  $\text{NH}_4\text{OH}$  concentration; volumetric ratio between the two solutions; precipitation temperature. The range within which these parameters were changed was:

HCl concentration:	1 - 11M
NH <sub>4</sub> OH concentration in the Na <sub>2</sub> WO <sub>4</sub> solution:	0 - 8M
V <sub>HCl</sub> /V <sub>Na<sub>2</sub>WO<sub>4</sub></sub> + V <sub>NH<sub>4</sub>OH</sub> :	0.09 - 1
Precipitation temperature:	-5 - 20 °C.

TABLE 1

Values of the variable parameters for the preparation of H<sub>2</sub>WO<sub>4</sub>(A) and H<sub>2</sub>WO<sub>4</sub>(B)

Variable parameter	Values for the preparation of	
	H <sub>2</sub> WO <sub>4</sub> (A)	H <sub>2</sub> WO <sub>4</sub> (B)
HCl concentration (M)	2.1	5.5
NH <sub>4</sub> OH* concentration (M)	0.1	3.6
$\frac{V_{HCl}}{V_{Na_2WO_4} + V_{NH_4OH}}$	0.09	0.75
Temperature (°C)	2	2

\*The pH values of the alkaline Na<sub>2</sub>WO<sub>4</sub> solutions in which H<sub>2</sub>WO<sub>4</sub>(A) and H<sub>2</sub>WO<sub>4</sub>(B) are precipitated are 10.9 and 11.7, respectively.

In order to simplify the experiments the Na<sub>2</sub>WO<sub>4</sub> concentration was kept constant at 0.05M. This value was selected on the basis of preliminary experiments, which showed that acids which are precipitated from diluted tungstate solutions display a larger specific surface.

Some of the experiments yielded acids with surface areas of over 70 m<sup>2</sup>/g. Supplementary experimental runs, carried out at the values of the parameters which give acids with maximum surface, showed the possibility of obtaining two distinct maxima: H<sub>2</sub>WO<sub>4</sub>(A) (Fig. 1) and H<sub>2</sub>WO<sub>4</sub>(B) (Fig. 2) using the intersection of the curves: surface area of the acid *vs.* one of the parameters (keeping the others constant). The respective values of these parameters are given in Table 1.

Figures 1 and 2 show that the two maxima are quite apart from each other in the multidimensional space formed by the variable parameters. The rest of the experimental points dispersed within this space do not suggest the presence of another similar maximum, since their values along the Z axis (Figs. 1 and 2) do not surpass 25 m<sup>2</sup>/g.

Thus, the first goal of this paper is reached — the determination of the values of the parameters which give the white modification of tungstic acid with a large specific area.

#### *Physical characteristics of the synthesized acids*

The following physical characteristics of the prepared acids were determined: surface area by BET tests with low temperature nitrogen adsorption; grain size determined by sedimentation analysis [14]; crystal habit of the

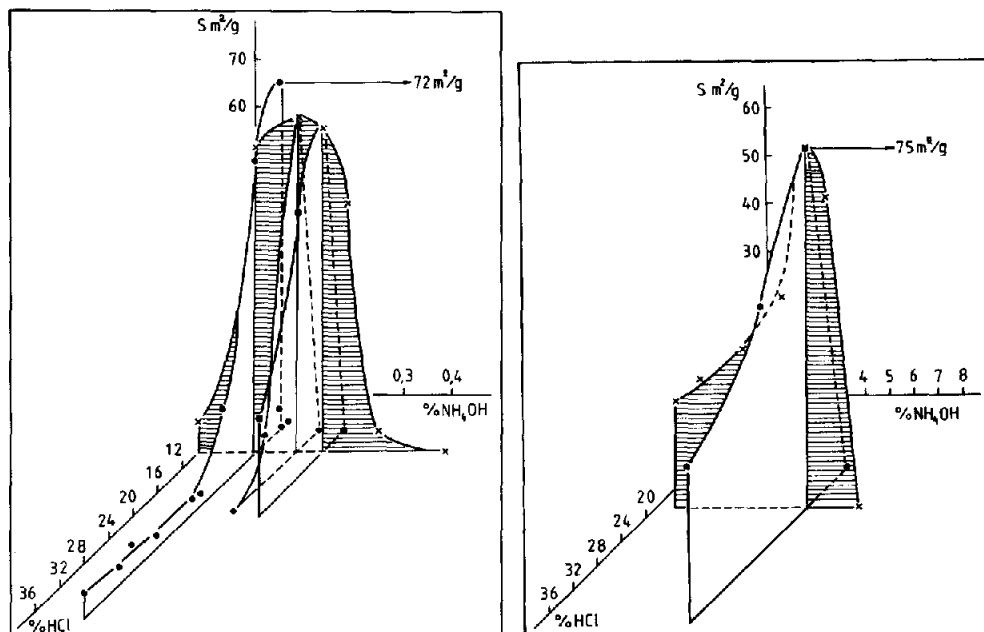


Fig. 1. (left) Relationship between the surface area of  $H_2WO_4$  and the values of the variable parameters (condition A).

Fig. 2. (right) Relationship between the surface area of  $H_2WO_4$  and the values of the variable parameters (condition B).

particles, using s.e.m. and t.e.m. micrographs taken with a JEOL, type SEM 100 B electronic microscope.

The BET measurements show that the surface area of the samples varies within a wide range from 4 - 5  $m^2/g$  to 76 - 80  $m^2/g$ . The sedimentation analysis gave rather surprising results, since all samples, regardless of specific surface, displayed a similar grain size (Fig. 3), with only one exception — the "B" acid with maximum surface. The grains of the latter are coarse as compared with the other samples. The results suggest that these acids do not display a relationship between surface area and grain size.

The s.e.m. photographs also do not show any substantial difference in the size and crystal habit between acid particles with specific surfaces of 10 and 70  $m^2/g$  both for the "A" and "B" acids (Fig. 4).

Differences in the structure of the particles of the acids with different surface areas are observed only in the t.e.m. photographs at high magnifications, over 50 000. They show that the particles of all acids with large specific surfaces, both "A" and "B", are porous and needle-shaped, while acids with small specific surfaces comprise compact and porous particles with a granular structure (Fig. 5). It can be concluded that the surface area of the white modification  $H_2WO_4$  samples we have investigated depends only slightly on

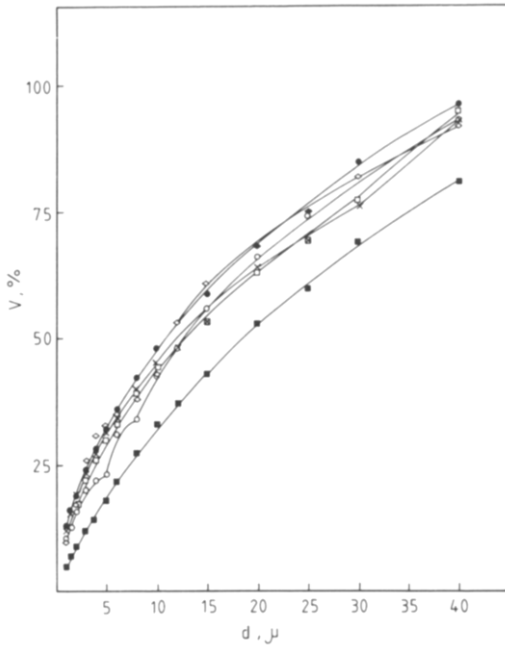
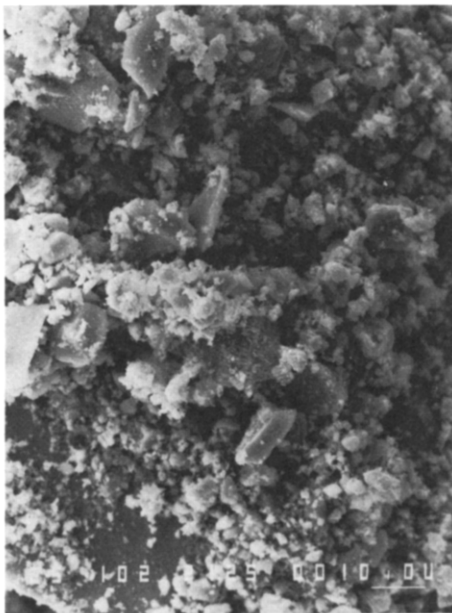
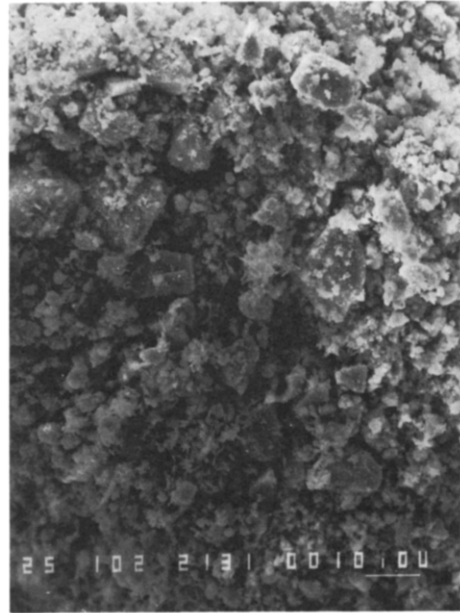


Fig. 3. Grain size distribution of  $\text{H}_2\text{WO}_4$  with different surface areas.  $\blacklozenge$ ,  $S = 10 \text{ m}^2/\text{g}$ ;  $\circ$ ,  $S = 55 \text{ m}^2/\text{g}$ ;  $\bullet$ ,  $S = 81 \text{ m}^2/\text{g}$  (condition A);  $\square$ ,  $S = 7.5 \text{ m}^2/\text{g}$ ;  $\times$ ,  $S = 58 \text{ m}^2/\text{g}$ ;  $\blacksquare$ ,  $S = 72 \text{ m}^2/\text{g}$  (condition B).

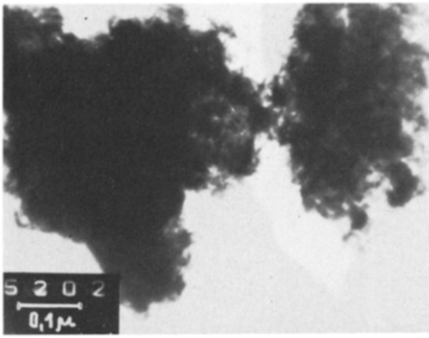


(a)

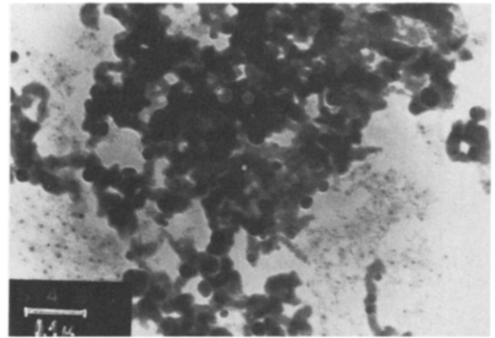


(b)

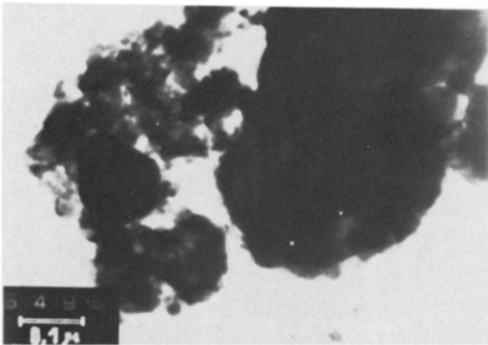
Fig. 4. S.E.M. photographs of  $\text{H}_2\text{WO}_4$  with different surface areas. (a)  $S = 10 \text{ m}^2/\text{g}$ ; (b)  $S = 70 \text{ m}^2/\text{g}$ . (Magnification  $\times 6000$ .)



(a)



(b)



(c)

Fig. 5. T.E.M. photographs of  $\text{H}_2\text{WO}_4$  with different surface areas. (a)  $S = 70 \text{ m}^2/\text{g}$ ; (b) and (c)  $S = 10 \text{ m}^2/\text{g}$ . (Magnification  $\times 100\,000$ .)

grain size, and is determined basically by the structural features of these particles.

The t.e.m. photographs at very high magnifications ( $\times 50\,000$ ) also display some differences between acids with large specific surfaces prepared under different conditions ("A" and "B") — Fig. 6. When juxtaposed, the photographs show that acids prepared under "A" conditions have a more distinct crystal structure.

#### *Synthesizing tungsten carbides from the prepared acids*

The next stage of the investigation was the synthesis of high surface area tungsten carbides from the acids obtained. This was accomplished by using high surface area (over  $60 \text{ m}^2/\text{g}$ ) acids, since it is well known from the literature, that the surface of the synthesized carbides is directly proportional to the surface of the initial raw materials. As shown by Böhm, Palanker and Svata [4, 5, 7] and by our results, the other parameters affecting the carbides obtained are temperature and duration of carburization.

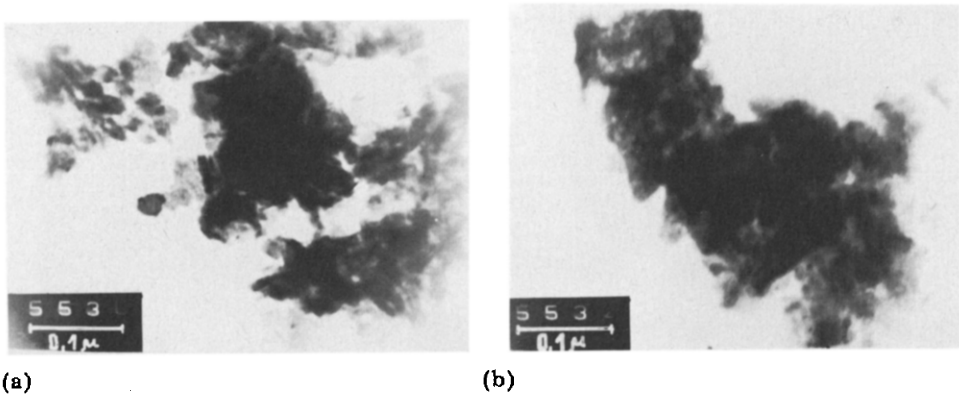


Fig. 6. T.E.M. photographs of  $H_2WO_4$  prepared under different conditions. (a)  $H_2WO_4(A)$ ; (b)  $H_2WO_4(B)$ .

If the process is carried out at more elevated temperatures and longer durations, the surface of the synthesized tungsten carbide decreases. Most of the authors quote 750 - 850 °C [4, 6, 7] carburization temperature and 2 - 6 h duration as the optimum conditions. Some authors show that at temperatures lower than 750 °C carburization is incomplete [4, 7]. A complete carburization during a synthesis carried out at 700 °C for 4 h has been reported only by Ross [8].

The use of "B" type acids and an increase in the CO flow rate during carburization from 20 - 30 to 80 - 90 l/h gave us the possibility of preparing carbides at 660 - 680 °C for rather short (90 - 100 min) periods. The surface area of the carbides obtained was within the range 22 - 26 m<sup>2</sup>/g. Figure 7 shows the profound change of the surface area of similar carbides, depending on the synthesis temperature which have been used hitherto [15]. The respec

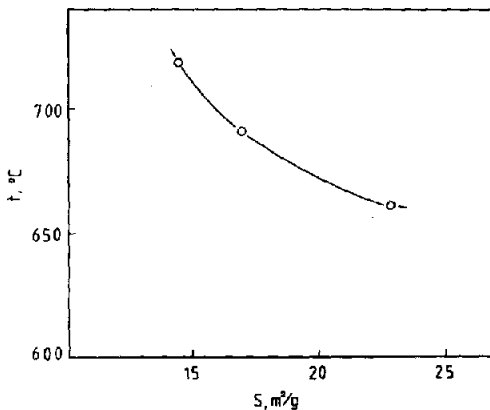


Fig. 7. Relation between the surface area of WC synthesized from  $H_2WO_4(B)$  and the synthesis temperature.

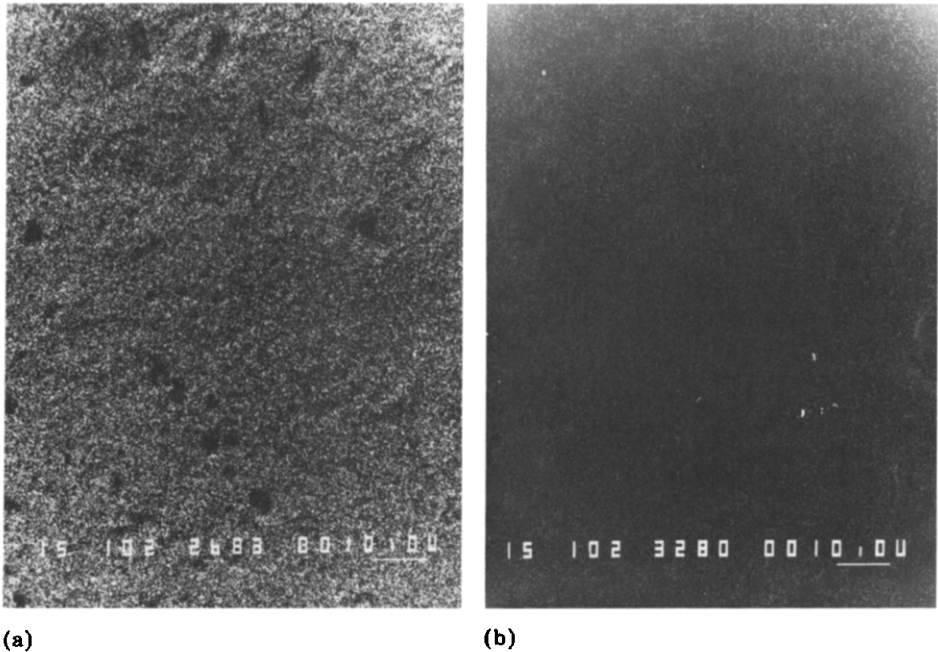


Fig. 8. X-ray maps showing  $O_2$  distribution on the surface of WC after degassing at different temperatures: (a) 50 °C; (b) 300 °C.

tween 660 and 720 °C. At temperature lower than 660 °C the samples contain unreacted tungsten.

Syntheses carried out under identical conditions, but using "A" type acids gave poor results with a specific surface less than 4 m<sup>2</sup>/g.

#### *Determination of the characteristics of the carbides obtained*

The following characteristics of the synthesized carbides were determined: composition of the sample (X-ray diffraction patterns), surface area (BET) by low temperature nitrogen adsorption, oxygen content in the surface layers (electron microscope JEOL Super Probe 733), t.e.m. photographs of the particle structure, and electrochemical activity in regard to the evolution and oxidation of hydrogen by methods described previously [10, 15].

The X-ray diffraction patterns show that the carbides synthesized from "B" type acids are free from tungsten impurities, while samples prepared from "A" type acids under identical conditions contain unreacted tungsten.

Experimental data show that the surface area of carbides prepared from "B" type acids depends on the temperature of degassing during the BET measurements, and the specific surface area figures of 16 - 18 m<sup>2</sup>/g when degassing is carried out at 50 °C increase to 22 - 26 m<sup>2</sup>/g if the process proceeds at 300 °C. The investigation of the surface with the JEOL Super Probe 733 clarified the reason for this discrepancy.



Figure 8 shows the distribution of oxygen on the surface of a tungsten carbide sample (10 days following the synthesis) after 2 h degassing in a nitrogen atmosphere at 50 °C (a), and at 300 °C (b). The recorder of the microprobe does not detect any oxygen in samples degassed at 300 °C, so that the points observed in photograph (b) must be accepted as background. If we juxtapose the two photographs, it becomes clear that after degassing at 50 °C a large portion of the surface is still covered with chemisorbed oxygen, which prevents the adsorption of nitrogen, hence the measured surfaces are smaller.

The t.e.m. photographs show that the particles of large surface area (24 - 26 m<sup>2</sup>/g) carbides, prepared using "B" type acids, display a structure similar to that of the particles of the initial raw materials (Fig. 9(a)). The decrease of the surface when synthesis is carried out at higher temperatures is accompanied by an agglomeration of the particles (Fig. 9(b)). The photo-

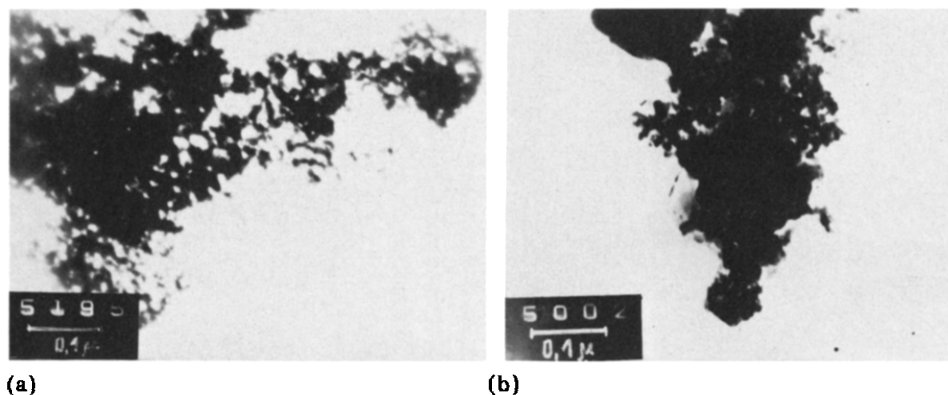


Fig. 9. T.E.M. photographs of WC prepared from H<sub>2</sub>WO<sub>4</sub>(B) at different synthesis temperatures: (a) 660 °C; (b) 720 °C.

graphs of carbides prepared from "A" type acids show that during synthesis, besides the agglomeration of particles (Fig. 10(a)), coarse crystals with smooth faces are also formed (Fig. 10(b), (c)). The presence of numerous similar species probably leads to the decrease of the surface area of these carbides. The changes which occur in the acid particles prepared under "A" conditions during the synthesis process are probably due to the differences in the respective crystal habits.

The activity of each synthesized carbide sample with regard to the evolution and oxidation of hydrogen in N H<sub>2</sub>SO<sub>4</sub> was determined in an effort to evaluate their electrochemical properties. The specific catalytic activity is determined per unit BET surface. With respect to the hydrogen evolution process the activity is equal to that of carbides synthesized from W<sub>4</sub>O<sub>11</sub>, and is substantially higher than figures for carbides synthesized from acids of surface area  $S = 30 \text{ m}^2/\text{g}$  which have been used hitherto [15]. The respective values at  $\phi = -80 \text{ mV}$  are shown in Table 2.

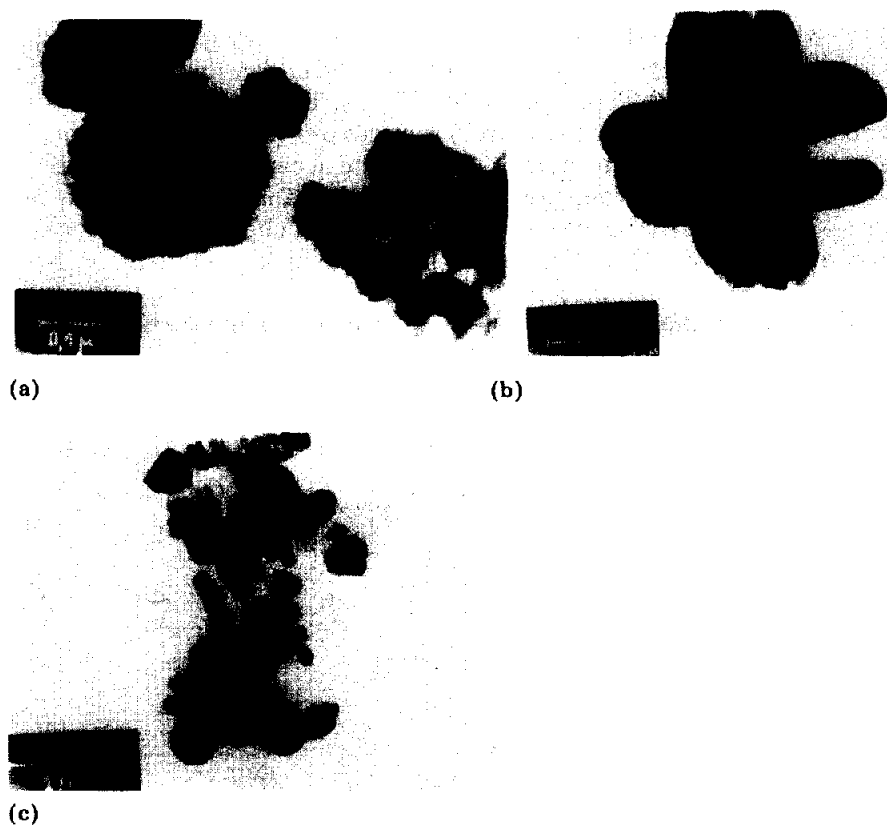


Fig. 10. T.E.M. photographs of WC prepared from  $\text{H}_2\text{WO}_4(\text{A})$ .

TABLE 2

Specific catalytic activity with respect to the hydrogen evolution in 1N  $\text{H}_2\text{SO}_4$  ( $T = 20^\circ\text{C}$  at  $\phi = -80$  mV (SHE)) of tungsten carbides prepared from the acid described and the raw material used in ref. 15

Raw material	Number of investigated samples	$i$ ( $\mu\text{A}/\text{cm}^2$ ) (BET)
$\text{W}_4\text{O}_{11}$	5	0.40 - 0.50
$\text{H}_2\text{WO}_4$ (30 $\text{m}^2/\text{g}$ )	7	0.20 - 0.28
$\text{H}_2\text{WO}_4$ (70 $\text{m}^2/\text{g}$ )	32	0.38 - 0.57

Due to the large surface area, carbides synthesized from the new acid display the highest activity per unit weight of the catalyst, which is very important for practical applications (Table 3).

TABLE 3

Catalytic activity with respect to the hydrogen evolution in 1N H<sub>2</sub>SO<sub>4</sub> ( $T = 20\text{ }^{\circ}\text{C}$  at  $\phi = -80\text{ mV (SHE)}$ ) of tungsten carbides prepared from the acid described and the raw material used in ref. 15

Raw material	Number of investigated samples	$i$ ( $\mu\text{A/mg}$ )
W <sub>4</sub> O <sub>11</sub>	5	55 - 60
H <sub>2</sub> WO <sub>4</sub> (30 m <sup>2</sup> /g)	7	20 - 40
H <sub>2</sub> WO <sub>4</sub> (70 m <sup>2</sup> /g)	32	68 - 150

However, with regard to the anodic reaction, the carbides synthesized by us displayed a lower specific activity than that of carbides prepared from W<sub>4</sub>O<sub>11</sub>, as shown by the experimental data (Table 4).

TABLE 4

Specific catalytic activity with respect to the hydrogen oxidation in 1N H<sub>2</sub>SO<sub>4</sub> ( $T = 20\text{ }^{\circ}\text{C}$  at  $\phi = 80\text{ mV (SHE)}$ ) of tungsten carbides prepared from the acid described and the raw material used in ref. 10

Raw material	Number of investigated samples	$i$ ( $\mu\text{A/cm}^2$ ) (BET)
W <sub>4</sub> O <sub>11</sub>	8	0.20 - 0.25
H <sub>2</sub> WO <sub>4</sub> (30 m <sup>2</sup> /g)	9	0.06 - 0.09
H <sub>2</sub> WO <sub>4</sub> (70 m <sup>2</sup> /g)	5	0.10 - 0.13

The reason for these differences between the anodic and cathodic catalytic activities is the decreased corrosion resistance of the carbides synthesized by us. The investigations show that the carbide is slowly oxidized even by atmospheric oxygen. This poor corrosion resistance does not affect the cathodic process, which proceeds at negative potentials in the presence of hydrogen, but is crucial in anodic processes. Therefore these carbides are convenient as catalysts for hydrogen evolution electrodes, while their virtues when used in the manufacture of hydrogen oxidation electrodes need further experimental evaluation of the changes which occur in the catalyst under working conditions.

## Conclusions

Conditions have been determined for the preparation of the white H<sub>2</sub>WO<sub>4</sub> modification with a large surface area (60 - 70 m<sup>2</sup>/g), and it is shown that this parameter depends mainly on the structure of the particles. It has been established that the relationship between the surface of the synthesized

carbides and the surface of the initial acid is ambiguous. Carbides of substantially different surface area (4 and 25 m<sup>2</sup>/g) are obtained from acids with similar surface areas (70 m<sup>2</sup>/g) but different particle habits, under identical synthesis conditions.

Carbides synthesized at low temperatures (660 - 680 °C) display a high catalytic activity with regard to the hydrogen evolution reaction. Their activity towards the anodic process is suppressed by the poor corrosion resistance.

## References

- 1 H. Bohm and F. A. Pohl, *Wiss. Ber. AEG-Telefunken*, 41 (1968) 46.
- 2 H. Bohm and D. Bagonz, *Ger. Offen. 1916340* (1971).
- 3 K. Mund and R. W. Schulte, *Ger. Offen. 1939127* (1971).
- 4 H. Bohm and F. A. Pohl, III. *J. Int. d'Etude des Piles à Combustible VI*, 1969, *Bruxelles*, p. 183.
- 5 M. Svatá and Z. Zabransky, *Collect. Czech. Chem. Commun.*, 39 (1974) 1015.
- 6 R. Fleischman and H. Bohm, *Electrochim. Acta*, 22 (1977) 1123.
- 7 V. Palanker, D. Sokolsky, E. Mazulevsky and E. Baybatyrov, *J. Power Sources*, 1 (1976/77) 169.
- 8 P. N. Ross and P. Stonehart, *J. Catal.*, 48 (1977) 42.
- 9 H. Biehler, *Ann. Chim.*, 2 (1947) 489.
- 10 I. Nikolov, V. Nikolova, T. Vitanov and M. Svatá, *J. Power Sources*, 4 (1979) 65.
- 11 G. F. Huttig and B. Kurres, *Z. Anorg. Chem.*, 122 (1922) 44.
- 12 G. F. Huttig and B. Kurres, *Z. Anorg. Chem.*, 126 (1923) 171.
- 13 A. M. Morley, *J. Chem. Soc.*, (1930) 1988.
- 14 Classification of method for determining particle size, *Analyst*, 88 (1963) 156.
- 15 I. Nikolov, T. Vitanov and V. Nikolova, *J. Power Sources*, 5 (1980) 197.