

HIGHLY DISPERSED TUNGSTEN CARBIDE FOR FUEL CELLS WITH AN ACIDIC ELECTROLYTE

V. Sh. PALANKER, D. V. SOKOLSKY, E. A. MAZULEVSKY and E. N. BAYBATYROV
Institute of Organic Catalysis and Electrochemistry, Alma-Ata (U.S.S.R.)

(Received February 25, 1976)

Summary

A technique for the preparation of highly dispersed tungsten carbide, useful as a catalyst for hydrogen electrodes in acidic electrolyte fuel cells, has been developed, and the properties of this material have been investigated. Optimum conditions for obtaining highly dispersed tungstic acid have been found, the latter being employed as a starting material for the synthesis of highly dispersed tungsten carbide. By optimization of the synthesis conditions a tungsten carbide of specific surface up to $30 \text{ m}^2/\text{g}$ has been obtained. This tungsten carbide has been used as a catalyst for hydrogen electrodes. At a potential of 200 mV and 90°C , a current density of $170 \text{ mA}/\text{cm}^2$ has been reached. It has been shown that in H_2SO_4 polarization of the hydrogen electrode at a potential above 300 mV for quite a long time increases the current on the tungsten carbide electrodes, instead of decreasing it.

Introduction

Since their discovery of the catalytic activity of tungsten carbide for hydrogen ionization in acid solutions, Böhm and Pohl [1] have published further papers dealing with the optimization of this catalyst and electrodes based on it. Although tungsten carbide is less active than platinum metals, it has an important advantage – a unique ability to resist very strong catalytic poisons, such as carbon monoxide, hydrocarbons and hydrogen sulphide. This allows tungsten carbide electrodes to operate on non-purified conversion gas, a property which is very important in the development of inexpensive fuel cells [2, 5]. Our investigations have shown that this immunity of tungsten carbide to poisoning is due to its complete inability to adsorb carbon monoxide and hydrocarbons [3] (hydrogen sulphide adsorption is also very poor [4]).

The aim of the present work is to find the optimum conditions for the synthesis of highly dispersed tungsten carbide and to investigate its catalytic activity, along with its other properties.

Experimental results and discussion

Preparation of highly dispersed tungstic acid

According to metallurgical procedures, tungsten and tungsten carbide are obtained from tungstic acid, but the specific surface of the latter is very small (2 - 3 m²/g). Thus, the present work commenced with the preparation of highly dispersed tungstic acid. This compound has a low solubility and is usually prepared by deposition with hydrochloric acid from a solution of sodium tungstate. Metallurgical experience shows that combining cold dilute solutions yields a white colloidal deposit of tungstic acid. This process has received little attention, since large crystals of acid, readily washed and filtered, are usually required.

In the present work, preliminary experiments have shown that the specific surface of tungstic acid is mainly affected by the concentration of the hydrochloric acid and tungstate solutions, by the volume ratio of these solutions and by the temperature of deposition. These parameters have been readily controlled by the use of standard glass instruments. Tungstic acid has been obtained by the following procedure: hydrochloric acid and sodium tungstate solution were continuously introduced into the reactor with vigorous stirring. The suspension of tungstic acid formed, having a low solubility, was continuously removed into a settler. The deposit thus obtained was washed 5 times with distilled water, using about 200 ml of water per 1 g H₂WO₄ each time. But even these multiple washes did not remove the sodium chloride completely, as was readily shown by a qualitative reaction with AgNO₃. A procedure was devised for more complete removal of sodium chloride. This involved a change of the tungstic acid to a colloidal state. The fivefold-washed tungstic acid was separated by centrifuging and dried at 100 ° - 120 °C to constant weight. The dry acid, mortar-ground to powder, was used for tungsten carbide preparation. The specific area was obtained from BET measurements using krypton or nitrogen.

The optimum values of the four main tungstic acid deposition parameters were determined, by the method of experimental design, to be: concentration of the Na₂WO₄ solution, 0.02 - 0.1 M; concentration of HCl, 10 - 11 M; volume ratio of hydrochloric acid to tungstate solution, 2 - 3; deposition temperature, 0 - 10 °C (a more convenient room temperature may also be used, though it involves a slight loss of specific surface). Under these conditions, a large number of experiments were carried out, yielding tungstic acid with a specific surface up to 80 m²/g.

Synthesis of tungsten carbide

Reduction of tungstic acid, with subsequent carburization, was carried out continuously in the same reactor. Hydrogen or carbon monoxide was used as the reductant and carbon monoxide for carburization. Reduction of highly dispersed tungstic acid proceeds via several steps. Adhesion of powder particles must be prevented, otherwise the phases which should be reduced at low temperatures will remain unreduced up to higher ones; under the latter

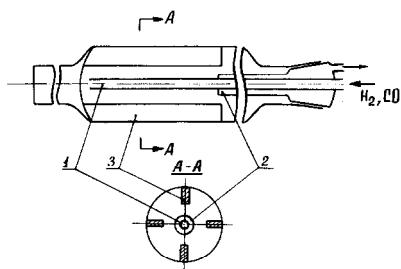


Fig. 1. Schematic diagram of a reactor for tungsten carbide preparation. 1, Gas inlet; 2, gas outlet; 3, ribs.

conditions the particles will be sintered more intensively. Particle adhesion can be prevented by employing a reactor of appropriate design, a proper amount of reactor charge, and a suitable gas flow rate to give good contact between powder and reducing gas.

A cylindrical quartz reactor (Fig. 1) of internal diameter 40 mm, with a reaction space 120 mm long, was employed in the experiments reported above. The interior of the reactor is ribbed for powder distribution. Tubes for gas inlet and outlet are mounted in the reactor lid. The reactor was held in a sloping position in an electric furnace and rotated by a reversible electric motor round a horizontal axis at 2 rev/min for the time of reaction. By changing automatically the direction of the reactor rotation after every 1 - 2 revolutions, we could eliminate the complex sealing of the connections to the gas inlet and outlet. We simply joined them to the lid with two rubber tubes, which rotated together with the reactor for 1 - 2 revolutions in either direction.

Tungstic acid was introduced in 20 - 25 g portions; reducing gas feed rate was 150 - 200 ml/min. Sampling was carried out at regular time intervals under an argon flow. The specific surface area was obtained from BET measurements and the phase composition by an X-ray method. The content of bonded carbon was found by burning the sample and adsorbing CO_2 in alkali. The amount of free carbon was determined by a colorimetric procedure [6] which is based on the fact that free carbon alone absorbs bromothymol blue [7].

The value of the specific surface of the carbide obtained is mainly determined by the rate of temperature increase and the composition of the reducing gas. A specific tungsten carbide surface of $12 \text{ m}^2/\text{g}$ was obtained by using pure carbon monoxide for reduction, as well as for subsequent carburization. In this case the temperature was raised according to Fig. 2 (curve 1). Changes in the specific surface area during reaction are shown by Fig. 3 (curve 1). The ratio of the specific surface of a sample taken at a given temperature to that of the initial tungstic acid is plotted on the ordinate axis. The final temperature of the experiment was fixed at 750°C as for short carburization times (5 - 6 h); this was the lowest value at which pure tungsten carbide (WC) was formed. Tens of hours were required even at 700°C , and the tungsten carbide formed still contained W_2C .

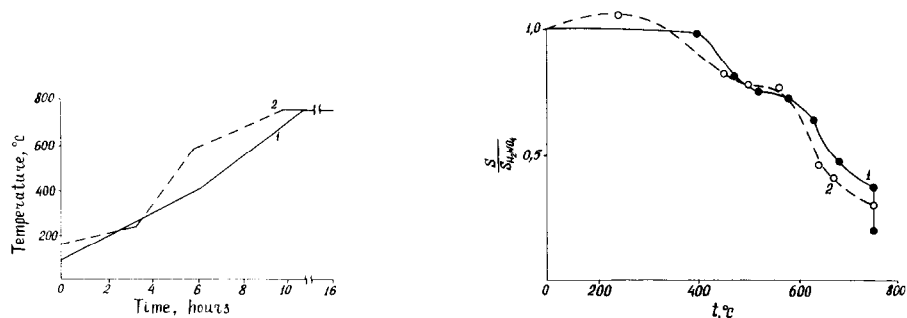


Fig. 2. Temperature increase during tungstic acid reduction and subsequent carburization. 1, The whole reaction proceeds in a CO atmosphere; 2, in H_2 up to $550^\circ C$, then in CO.

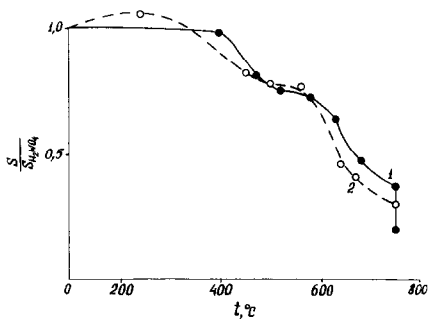


Fig. 3. Relative change in specific surface during reduction and carburization. S = specific area of sample at $t^\circ C$; $S_{H_2WO_4}$ = initial specific area of tungstic acid.

1, The whole reaction proceeds in a CO atmosphere; 2, in H_2 up to $550^\circ C$, then in CO.

Carburization with pure carbon monoxide almost always involves free carbon deposition on the tungsten carbide surface, due to the thermodynamic instability of carbon monoxide at temperatures below $1000^\circ C$ and its deposition on certain catalysts, such as tungsten carbide. Attempts to employ mixtures of $CO + H_2$ or $CO + CO_2$ for carburization, in order to prevent deposition of free carbon, were unsuccessful. H_2 or CO_2 inhibits carburization to such an extent that tungsten carbide does not form even after long reaction times, e.g. over 20 h. The inhibiting action of CO_2 had been reported earlier by metallurgists, from studies on the reduction of other oxides, such as iron oxides.

Reduction of tungsten oxides with hydrogen proceeds much faster than with carbon monoxide. Finally, it was found best to use hydrogen at $550^\circ C$, then substitute pure carbon monoxide for hydrogen and bring the reaction to completion. The sequence of optimum temperature increases in this experiment is shown by Fig. 2 (curve 2); the change in the specific surface of the material during this reaction is given by Fig. 3 (curve 2). By this procedure, tungstic acid with a surface area of $60\text{ m}^2/\text{g}$ yielded tungsten carbide with a $20\text{ m}^2/\text{g}$ surface, whereas from tungstic acid with a $75 - 80\text{ m}^2/\text{g}$ surface, carbide with a $30\text{ m}^2/\text{g}$ surface was obtained. A slower temperature increase yields no additional specific tungsten carbide surface, since the decrease of the latter when passing from H_2WO_4 to WC approximates to the theoretical value, owing to increasing material density.

It has been already noted that carburization by carbon monoxide at temperatures below $1000^\circ C$ involves free carbon deposition on the carbide surface, thus decreasing the catalyst activity. The use of hydrogen for free carbon removal gave optimum results; hydrogen was admitted to the reactor, after carburization, at $750^\circ C$, and the free carbon was removed from the surface as hydrocarbons in 3 - 4 h. This could be verified analytically [6].

Electrocatalytic properties of highly dispersed tungsten carbide

Figure 4 shows polarization curves for hydrogen oxidation on a hydrophilic gas diffusion electrode, contacting an asbestos membrane saturated

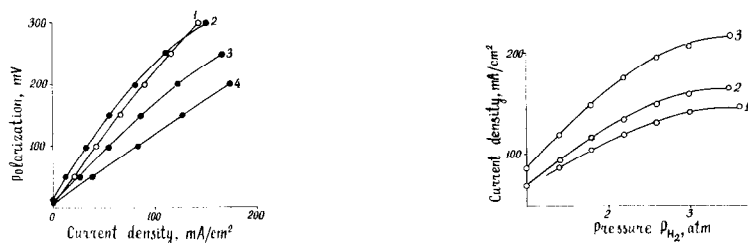


Fig. 4. Polarization curves for hydrogen oxidation on tungsten carbide electrodes. WC content = 120 mg/cm^2 . 1, 40% H_3PO_4 , $t = 90^\circ\text{C}$; 2, 3, 4, 30% H_2SO_4 at 50° , 70° and 90°C , respectively. H_2 excess pressure, 2.5 atm.

Fig. 5. Dependence of the H_2 oxidation current on H_2 pressure at 300 mV and 90°C . WC content, 120 mg/cm^2 . 1, 40% H_3PO_4 ; 2, 30% H_2SO_4 , without anodic treatment; 3, 30% H_2SO_4 , after anodic treatment.

with sulphuric or phosphoric acid. This and the subsequent Figures show the current densities related to the geometrical electrode surface. As in previous work [5], we obtained high current densities, quite suitable for industrial fuel cells. The dependence of current densities on hydrogen pressure is shown in Fig. 5. It has been previously found that the current is directly proportional to hydrogen pressure on smooth tungsten carbide [8] and thin gas-diffusion electrodes (up to 40 mg WC/cm^2). Thick electrodes ($100 - 120 \text{ mg WC/cm}^2$), on which high current densities can be obtained, do not operate under strictly kinetic conditions. On our electrodes, therefore, a current limit was reached at a certain pressure (about 3 atm.). This limit can be increased by improving the electrode structure.

Figure 5 (curves 2 and 3) shows different states of one electrode. Curve 3 was obtained after electrochemical activation of the electrode. It has been noted earlier, that anodic treatment of a tungsten carbide electrode at a potential of about 700 mV in the presence of a reductant increases its activity [9]. We found that a substantial increase in current on tungsten carbide electrodes by anodic polarization may be achieved only in a H_2SO_4 solution, in the presence of H_2 . In phosphoric acid, anodic treatment produces very little effect, whereas in hydrochloric acid, it even decreases the current.

Figure 5 shows the slight initial difference between the current densities in H_2SO_4 and H_3PO_4 . After anodic polarization, however, the current in H_3PO_4 remained unchanged, whereas it rose by about 1.5 times in H_2SO_4 . Repeated experiments with H_2SO_4 and H_3PO_4 yielded the same, quite well reproducible, results. The difference between the curves for H_2SO_4 and H_3PO_4 at the same temperature (90°C) is shown as a maximum current on the electrodes (Fig. 4).

It was also found that the electrodes were "activated" in H_2SO_4 at any potential in the range of 300 - 700 mV, not only at 700 mV. In region (a), Fig. 6, the electrodes were maintained at $\varphi = 300 \text{ mV}$ for 3 h; the current on the electrodes rose all this time continuously and reached a limit in 2 - 3 h. Then these electrodes were polarized at 700 mV for 0.5 - 1 h. After switching off the potentiostat for 2 - 3 min, the electrodes were polarized at 300 mV

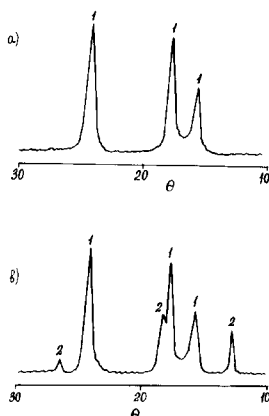
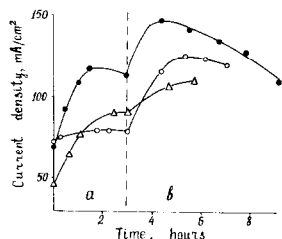


Fig. 6. Variation in current density during hydrogen oxidation at 300 mV on three tungsten carbide samples: (a) maintained at 300 mV continuously, (b) after anodic treatment at 700 mV for the time shown on the abscissa. WC content, 40 mg/cm². 30% H₂SO₄, $t = 90^{\circ}\text{C}$, excess $P_{\text{H}_2} = 1.2$ atm.

Fig. 7. Diffraction patterns of tungsten carbide before (a) and after (b) polarization at 700 mV in H₂ atmosphere. 1, WC; 2, WO₂.

and the current was recorded. These current values are quoted as points in region (b), Fig. 6. After a while, a current limit was reached also here, and further polarization at 700 mV led to a decrease in electrode activity.

When a maximum current had been reached, some electrodes were taken out of the cell, washed, and dried; then X-ray patterns were recorded, and the specific surface area was determined as well. One of these X-ray patterns is shown in Fig. 7, along with that of tungsten carbide which had not been polarized, but was washed and dried in the same manner. It may be seen that at 700 mV, a certain amount of WO₂ appeared in the sample; a quantitative evaluation has shown that the content of the oxide amounts to 10% of the WC content. These experiments show clearly that a portion of the tungsten carbide oxidizes during anodic polarization.

The current increase on tungsten carbide electrodes after anodic treatment may be due to (a) an increase in the specific activity of the catalyst during oxide formation, and (b) an increase in the specific surface area because of reduction of the catalyst particle size during oxidation. Up to now the activity increase has been interpreted as an increase in the specific activity, but the catalyst surface has never been measured after anodic treatment.

By determining the catalyst surface before and after anodic treatment of the electrodes we have found that the increase in the hydrogen oxidation current in H₂SO₄ involves a simultaneous proportional increase in the catalyst surface, so that the specific activity remains unchanged. Anodic treatment in phosphoric acid involves no essential change in the catalyst surface and no current increase.

Occasional large anodic electrode potential steps during operation of the current source are harmless to tungsten carbide, since surface oxidation in this

case only contributes to an increase in current. The extent of carbide oxidation is large enough to involve a high catalytic activity of the electrode, so that the latter can withstand the anodic potential steps for a long period. Figure 6 shows that even after continuous polarization at 700 mV for several hours the electrodes retain their high activity.

Some properties of highly dispersed tungsten carbide differ from those of poorly dispersed WC powder prepared by metallurgists. The composition of metallurgical carbide prepared at about 1500 °C corresponds exactly to that of WC containing 6.12 wt.% C, whereas highly dispersed carbide prepared at 750 - 800 °C contains less than 6 wt.% carbon. Some authors [10 - 12] consider carbon deficiency as the cause for the elevated catalytic activity of highly dispersed tungsten carbide, ascribing this phenomenon to its defective structure [11, 12]. But in these studies, activity has been determined from given catalyst portions, without considering the large difference between the specific surface areas of the various samples. In our numerous experiments, we compared the specific catalytic activity (per unit true BET area) of industrial carbide ($S = 0.1 \text{ m}^2/\text{g}$) with that of highly dispersed ($10 - 20 \text{ m}^2/\text{g}$) and smooth tungsten carbide. The results suggested no substantial differences between the specific activities of these carbides.

This may be interpreted as follows: during the transition to steady-state working conditions, the surface states of all the carbide samples become similar, so that the part played by total volume content of carbon in the carbide and the extent of the lattice disorder in the bulk of the catalyst particle may be of little importance. This factor can affect the mechanical properties of the material, as well as the electroconductivity and other bulk properties, without apparently changing the surface properties, the latter being similar in all the carbide samples. That is why we associate the total increase in tungsten carbide activity, when substituting highly dispersed samples for poorly dispersed ones, with an increase in the specific catalyst surface.

It should be pointed out, however, that our polarization curves were obtained from tungsten carbide which had been in contact with air. At present there are no data on the activity of an absolutely pure non-oxidized WC surface.

References

- 1 H. Böhm and F. A. Pohl, *Wiss. Ber. AEG-Telefunken*, 41 (1968) 46.
- 2 F. A. Pohl, *Bull. Schweiz. Elektrotechn. Vereins*, 63 (1972) 910.
- 3 R. A. Gajjev, V. Sh. Palanker and D. V. Sokolsky, *Elektrokhimiya*, 11 (1975) 1340.
- 4 V. Sh. Palanker and R. A. Gajjev, *Elektrokhimiya*, 11 (1975) 1075.
- 5 L. Baudendistel, H. Böhm, G. Louis and F. A. Pohl, 23rd Meet. Int. Soc. Electrochem., Stockholm, (1972) 424.
- 6 D. V. Sokolsky, V. Sh. Palanker, E. A. Mazoulevsky, A. M. Khisametdinov and K. K. Kousembaev, *Trans. Inst. Org. Catal. Electrochem.*, Alma-Ata, 12 (1976) 92.
- 7 T. N. Nazarchuk and L. E. Pechentkovskaya, *Zavodskaya Labor.*, (3) (1961) 256.
- 8 D. V. Sokolsky, V. Sh. Palanker and E. N. Baybatyrov, *Electrochim. Acta*, 20 (1975) 71.

- 9 H. Binder, A. Köhling, W. Kuhn, W. Lindner and G. Sandstede, *Nature*, 224 (1969) 1299.
- 10 H. Binder, A. Köhling, W. Kuhn, W. Lindner and G. Sandstede, *Energy Convers.*, 10 (1970) 25.
- 11 M. Statá, Z. Zábranský, *Collect. Czech. Chem. Commun.*, 39 (1974) 1015.
- 12 M. Svatá and Z. Zábranský, *Powder Technol.*, 11 (1975) 183.