SEDIMENTED POWDER ELECTRODE
FOR STUDYING THE PROPERTIES
OF TUNGSTEN CARBIDE CATALYSTS

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A method was worked out for studying catalysts in the form of a body consisting of the powder only, sedimented on a golden grid.

Since 1968[1], tungsten carbide (WC) has been employed for the oxidation of hydrogen in fuel cells operating with an acid electrolyte. It has been found that the activity of the tungsten carbide catalyst is strongly dependent on the conditions of the synthesis[2]; since porous electrodes, as employed in a fuel cell, are unsuitable for studying the properties of a catalyst due to many side influences, a method was worked out, allowing to study the catalyst in the form of a body consisting of the powder only, sedimented on a golden grid. A deeper insight into the mechanism of the reaction was thus obtained.

EXPERIMENTAL

The catalyst employed was a tungsten carbide powder prepared by carburizing a mixture of the blue oxides of tungsten, obtained by decomposing the hexacarbonyl of tungsten in a reducing atmosphere[3]. The very fine powder thus obtained was carburated at 700°C for four and a half hours in a mixture of carbon monoxide and argon in the ratio 1 : 1. A highly voluminous powder was obtained with a surface area of $20 \, m^2/g$ and a high deficiency in carbon (5·47% against stoichiometry 6·12%). The deficiency in carbon (which, on the other side, was outbalanced by a high content of oxygen (3·15%)) manifests itself in a highly defective crystal lattice[4] which, it is believed, is the reason for the high catalytic activity observed.

The catalytic vessel is designed in Fig. 1. Working electrode A is represented by the catalyst sedimented on a golden grid placed in the lower part of Teflon cylinder D. The grid is placed on fritted glass E covered with filtration paper F. 200 mg of the catalyst were dispersed in electrolyte and introduced into cylinder D, stopcock G was closed, and a vacuum pump was connected in the place of reference electrode B. The electrolyte was then sucked through the fritted glass bringing the powder into close contact with the golden grid. The electrolyte was then admitted into the working compartment of the vessel by disconnecting the pump and opening stopcock G. Auxiliary electrode C was represented by a golden wire of 0·5 mm diameter.

To avoid oxidation of the catalyst and evolution of hydrogen, the potential region of $+100$ to $+300$ mV was selected. The electrolyte, $1 \text{N-}H_2SO_4$ at 20°C, was constantly bubbled through

with argon (oxygen content below 20 ppm). The measuring set-up consisted operatinoal amplifiers connected to a current-type recorder (EZ 2, Laboratorní přístroje, Prague). The potential was measured against a Hg/Hg_2SO_4 reference electrode; in the present paper, the values are converted to the standard hydrogen scale.

RESULTS AND DISCUSSION

The measurement consisted in registering, at controlled potential, the time change in the current density, induced by changing the potential in steps of 50 mV; at the same time, the total quantity of charge passing through was determined by an analogue current integrator. The dependence charge-potential is linear (Fig. 2); at $E \approx \approx 300$ mV, however, oxidation of the surface seems to occur, and the charge used up between the last two points increases. In the reverse direction, the establishment of the equilibrium is slow, and the attainment of the given coverage of the electrode would require long periods of time. For this reason, when proceeding in the negative direction, the electrode was always brought to the initial potential value of 100 mV (to ensure that the coverage of the surface be equal to that given in Fig. 2).

The experimental technique permitted measuring the maximum currents 0·6 s after the potential change. In Fig. 3, the dependences $I–E$ are depicted for three different initial coverage values. It may be seen that for the reduction currents, the dependences are exponential (curves A, B, C_1). The charge transfer coefficient β and the exchange current I_0 were calculated from Tafel curves and values of $\beta = 0·3$ and $\log I_0 = 1·05$ (in mA) were obtained. For the oxidation currents, there are
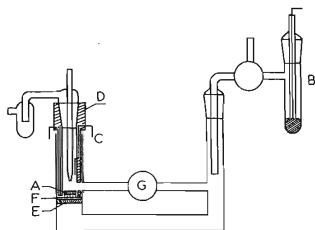

Fig. 1

Schematic Design of Measuring Set-up

   A Working electrode; B reference electrode; C auxiliary electrode; D teflon cylinder; E fritted glass; F filtration paper; G stopcock.
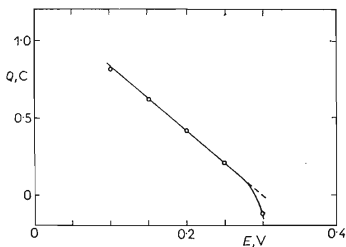
Fig. 2

Charge–Potential Curves of Sedimented Tungsten Carbide Powder Electrodes

deviations from the theoretical course (see curve G calculated for 100 mV initial potential value, $\alpha = 0.7$, and $\log I_0 = 1.05$ mA).

The linear course (in semilogarithmical coordinates) of the relation charge-time at constant potential together with the exponential course of the reduction current on the potential point to a first order reaction proceeding on a uniformly unhomogeneous surface. It may be assumed[5] that the current is determined by the reaction $H_2 \rightarrow 2 H_{ads}$. This apparently is followed by the step $2 H_{ads} = (H_2)_{ads}$. This would explain the quasi-linear course of the relation current–potential during the reverse process of the oxidation of hydrogen adsorbed on the electrode surface (Fig. 3, curves D, E, F). Since there was a 0.6 s interval between the measurement and the potential change, a certain amount of H_{ads} had time to undergo oxidation; consequently, the maximum current measured was influenced by the rate of both oxidation (this explains the deviation from the theoretical course — compare curves G and D in Fig. 3), and dissociation of $(H_2)_{ads}$. The dependence $\log Q$ vs time is, in this case, also linear.

Fig. 4 gives the dependence of the stationary currents of the oxidation of gaseous hydrogen on the same electrode. In this case, argon was substituted with hydrogen prepared in a stand-by electrolyzer. The current was allowed to reach a constant value. In comparison with the currents I_{max} of the oxidation of hydrogen adsorbed on the surface of the electrode, these values are about two orders of magnitude higher; this suggests that, on a tungsten carbide electrode, the oxidation of gaseous hydrogen proceeds at an almost equilibrium coverage of the surface (Fig. 2), the
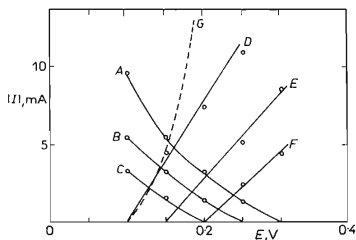

Fig. 3

Current–Potential Curves of WC Powder Electrodes at Three Different Initial Values of Coverage

   A, B, C reduction currents; D, E, F oxidation currents; G theoretical curve.
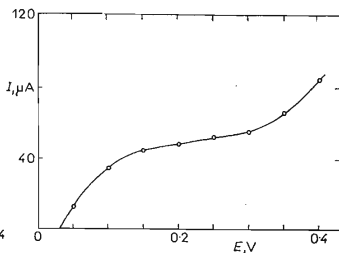
Fig. 4

Oxidation of Gaseous Hydrogen in Current––Potential Coordinates

rate determining step being the reaction $H_2 \rightarrow (H_2)_{ads}$. The adsorption activation energy, calculated from the curve current–temperature at constant potential, is $18-19$ kcal/mol which is somewhat higher than the values reported by Böhm[1] and Wiesener[6]. Assuming that the total surface of the electrode was participating in the reaction, the maximum specific charge consumed for oxidating hydrogen amounts to 20.8 $\mu C/cm^2$ which is in fair agreement with the value given by Sokolski and coworkers[7].

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