ADSORPTION AND ANODIC OXIDATION OF HYDROGEN ON TUNGSTEN CARBIDE ELECTRODES

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So far the anodic oxidation of hydrogen has mainly been performed in fuel cells working with an alkaline electrolyte. The drawbacks of an alkaline cell - carbonate formation and poisoning of the electrocatalysts - are however sufficiently well known.

Fuel cells working with an acid electrolyte avoid these difficulties. Noble metals however are needed as electrocatalysts. The resulting main disadvantages are the high inherent cost and the sensitivity of platinium against CO.

Our aim therefore was the utilisation of non-noble metal catalysts for the anodic oxidation of commercial, impure hydrogen in an acid fuel cell.

Four years ago we discovered that tungsten carbide is a useful electrocatalyst /1/. WC had so far been known in engineering as a refractory material with hard wearing properties. Catalytic properties had not until then been attributed to this substance. In view of its excellent acid resistance and good electrical conductivity we have prepared gas diffusion electrodes from WC-powder. On these electrodes, arranged in a conventional half-cell with 2 N H_2SO_4 as an electrolyte, we have measured the anodic hydrogen oxidation.

The first figure shows the results of the triangular voltage sweep measurements. With argon only at a potential exceeding 700 mV against a H_2 reference electrode in the same solution according to Giner /2/ commences the oxidation of the WC. With hydrogen higher current densities are achieved which are attributable to the anodic oxidation of hydrogen. Stationary measurements too - as in Figure 2 - show the hydrogen consumption rate. The results for different temperatures provide an activation energy in the range of 5.5 to 7.6 kcal/mol.

These measurements were taken on a gas diffusion electrode which was manufactured from a commercial quality of WC powder. But to exclude secondary effects such as porosity etc. measurements are best made with smooth WC electrodes. Such electrodes are obtained by carburizing 20µm thick tungsten foils with lampblack at temperatures of 1500-1600°C. A thicker sheet would not yield a full carburization effect. At these smooth electrodes the oxidation and adsorption of hydrogen was measured in a thermostatically controlled cell. Again a half-cell assembly was chosen with a platinized platinum electrode as the reference electrode, and 2N H_2SO_4 as the electrolyte. The hydrogen was streamed through a frit. (Fig. 3)

Only low current densities are observed at these smooth WC electrodes for the anodic hydrogen oxidation. At 20 µA/cm^2 the limiting current density is already found to occur. This is rather a low value compared to smooth platinum electrodes. The exchange current density for the H_2/H^+ reaction at WC is also very low, 0,4 µA/cm^2.

We have determined the kinetics of hydrogen adsorption under open circuit conditions by plotting the charging curves. For this

purpose the electrode is subjected to a loading cycle as is illustrated in Figure 4. First the electrode was kept at +400 mV where practically no H_2 adsorption takes place. Thereafter the electrode is placed into a potential-free state, and during this period of time t_{ad} hydrogen is being adsorbed. When this period has elapsed the whole amount of adsorbed hydrogen is oxidized by one rectangular current impulse; the adsorbed quantity of hydrogen is determined from the potential curve. By selecting various lengths of tad the maximum adsorbable hydrogen amount and the kinetics of the adsorption process may be determined.

A noticeable H_2 adsorption on the WC electrodes only occurs after several anodical impulses when the electrodes assume potentials of 800 to 1000 mV. It must therefore be assumed that adsorption does not directly proceed on the WC surface but rather on a thin oxide layer formed during the anodic impulse duration.

The maximum adsorbable hydrogen volume is not reproducible employing various smooth WC electrodes. The values found lay between 7 and 32 $\mu C/cm^2$. The platinum electrode in contrast yielded 570 $\mu C/cm^2$.

The adsorption process kinetics also differ between WC and Pt electrodes. This process may be characterized by the Langmuir equation:

$$\frac{d\theta}{dt} = kc_{H_2} (1 - \theta)^n$$

$$\log \frac{d\theta}{dt} = \log K + n \log (1 - \theta)$$

where θ represents the degree of coverage - θ is arbitrarily equated with unity for the maximum adsorbable H_2 amount - k is the rate constant, c_{H_2} the hydrogen concentration within the electrolyte, and n is the order of reaction with regard to the free surface sites.

Figure 5 shows log $d\theta/dt$ plotted over log $(1 - \theta)$. The slope of the curve and hence of the reaction order n are found to be unity for platinum, for tungsten carbide however two. The slope is very well reproducible for the diverse WC electrodes.

With platinum one surface site is needed, i.e. the adsorption of the H_2 molecule determines the rate of the reaction; with WC and reaction order 2, however, two surface sites are needed. The rate determining step here is the dissociation of the H_2 molecule:

$$H_{2ad} \longrightarrow 2\ H_{ad}$$

The two H atoms are then adsorbed on two surface sites; only with higher fractional coverages will values below 2 be found. With largely occupied surfaces also the adsorption of the H_2 molecule tends to determine the reaction rate.

In spite of the low exchange current density and the low adsorption capacity for hydrogen at smooth WC electrodes, higher current densities may also be attained with WC electrodes manufactured in a suitable process and under the right conditions. Carburization must then be carried out at as low a temperature as is possible with short reaction times. Another precondition is a small particle size.

A proven carburizing method is the reaction of tungsten powder (0,3 μ particle size) with CO at temperatures lying below 1000°C. This process takes place inside a rotating furnace tube; this yields uniform products.

The gas diffusion electrodes are manufactured from a thus prepared WC powder, and then the current-voltage characteristics are plotted for the anodic hydrogen oxidation.

In the Table Fig. 6 below the results are shown for a test series carried out at the flow rate of 5 l CO/h. The current density at U_H = 100 mV and the various phases are represented for different carburizing times and temperatures.

At 700°C and even prolonged reaction periods the tungsten powder fails to become fully carburized. But at 800° or at 900°C and within 6 or 8 hours a pure WC is produced. It is of interest to note here that the reaction proceeds via the phase $\alpha - W_2C$, while at 700°C no $\alpha - W_2C$ could be detected. The current densities are higher for the shorter reaction times; however with longer reaction times the catalytic activity drops. This is due to the precipitation of carbon on the catalyst surfaces.

The carbon content and hence the stoichiometry of the tungsten carbide are of great significance for the catalytic activity. Figure 7 shows the carbon content of the WC and the current density plotted against the reaction period, for a reaction temperature maintained at 800°C. By increasing the reaction period, the carbon content increases and exceeds the stoichiometric equivalent. The activity (current density), however, shows a peak. In Figure 8 the activity is plotted against the carbon content for the WC catalysts produced by CO carburization. It can be seen that all results lie within the region between the two curves. Because of the widely differing reaction conditions a range is obtained rather than a characteristic curve. This range, however, shows a distinct maximum. The WC catalysts develop their highest catalytic activity for a carbon content of 5.9 to 6.0 % wt. (theoretical value 6.12 %).

Figure 9 represents a current-voltage characteristic for the anodic oxidation of hydrogen which has been gained at such a sub-stoichiometric material. Current densities of 100 mA/cm^2 are obtained at a polarization of 260 mV.

Noteworthy is that such WC electrodes work on impure hydrogen without any risk of poisoning. Therefore it is possible to operate fuel cells with tungsten carbide anodes consuming unpurified steam reforming gas as their fuel source.

REFERENCES

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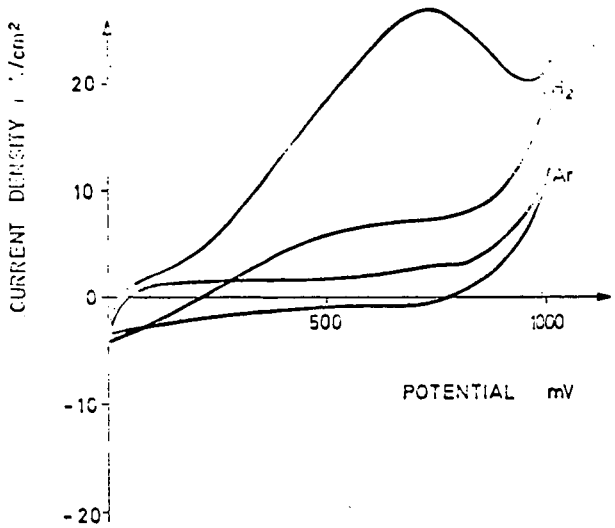

Fig. 1: Potentiodynamic current-potential curves at a WC gasdiffusion electrode, sweep speed 0,1 V/min

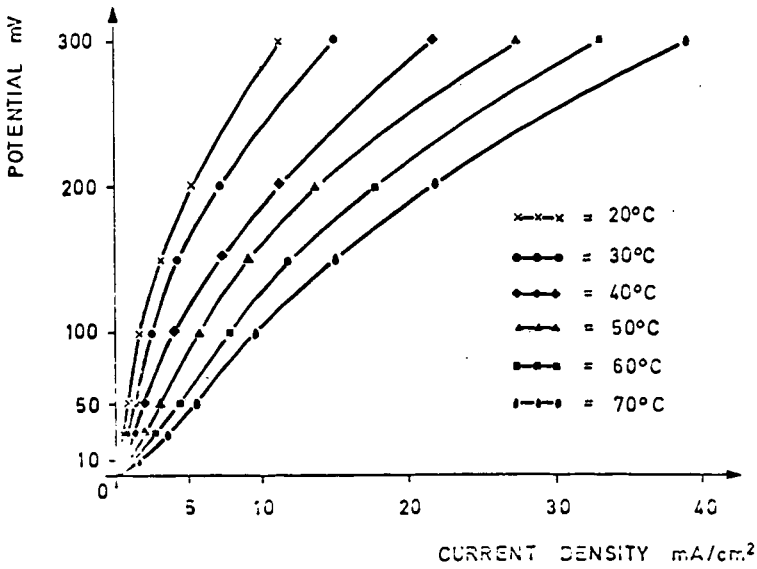

Fig. 2: Current-potential characteristics for the anodic oxidation of hydrogen at diffusion electrodes prepared from commercial WC

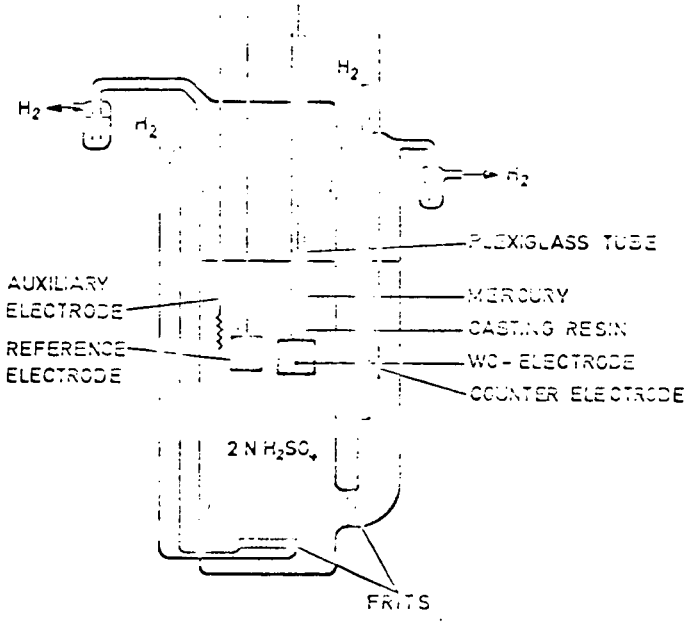

Fig. 3: Schematic diagram of cell

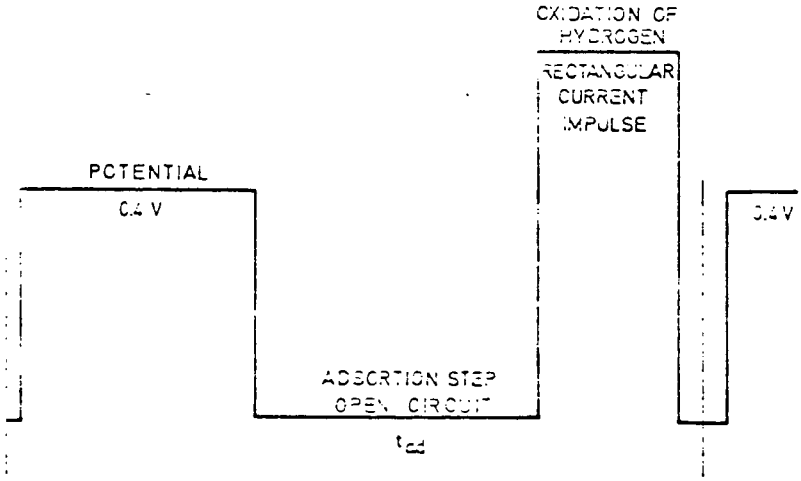

Fig. 4: Loading sequence for the hydrogen adsorption measurement

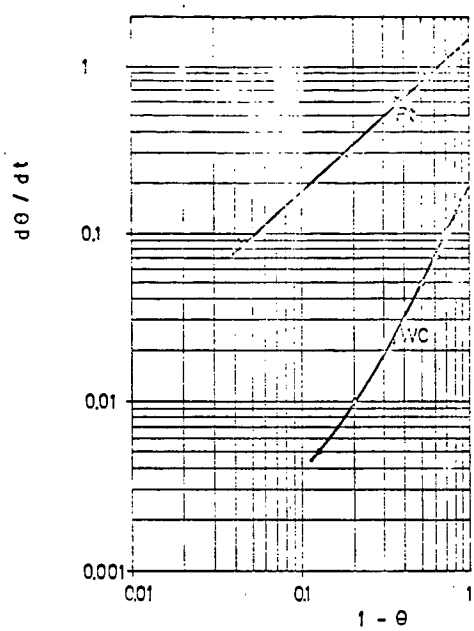

Fig. 5: log $\frac{d\theta}{dt}$ vs. log $(1 - \theta)$
for the adsorption of H_2 on Pt and WC at open circuit conditions

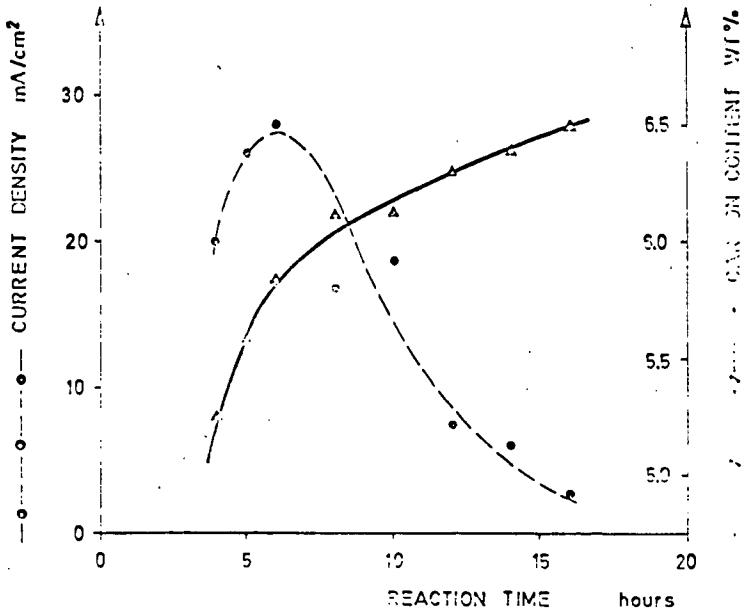

Fig. 7: Effect of carburizing time on the carbon content and on the current density (reaction temperature [illegible]

Reaction time hours	Reaction temperature 700°C	800°C	900°C
4	WC, W 24 mA/cm^2	WC, α-W_2C, W 20 mA/cm^2	WC, α-W_2C, W 6 mA/cm^2
6	WC, W 24 mA/cm^2	WC 27 mA/cm^2	WC, α-W_2C 14 mA/cm^2
8	WC, W 22 mA/cm^2	WC 16 mA/cm^2	WC 22 mA/cm^2
10	WC, W 15 mA/cm^2	WC 19 mA/cm^2	WC 19,5 mA/cm^2
12	WC, W 12 mA/cm^2	WC 6 mA/cm^2	WC 16 mA/cm^2
14	WC, W 12 mA/cm^2	WC 6 mA/cm^2	WC 14 mA/cm^2
16	WC, W 6 mA/cm^2	WC 2 mA/cm^2	—

Current densities were measured at $U_H = 100$ mV against the hydrogen electrode in the same electrolyte

Fig. 6: Effect of carburizing time and temperature on the catalytic activity of WC

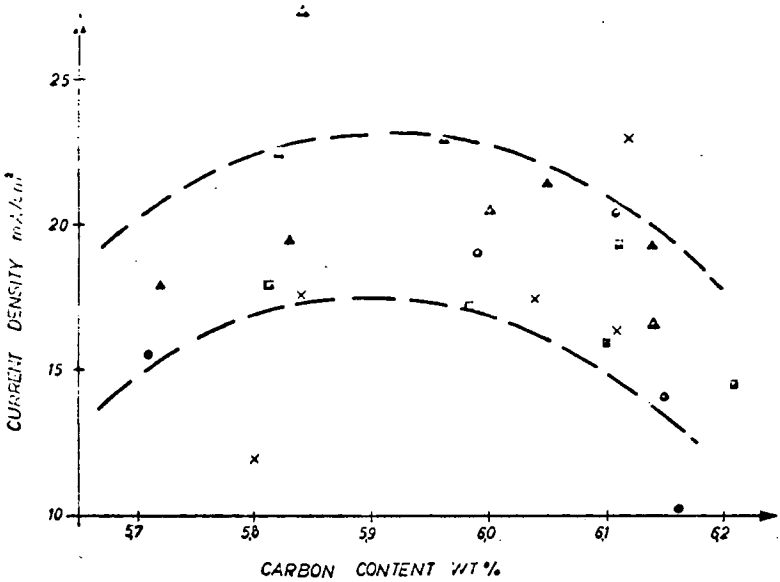

Fig. 8: Relationship between the current density at $U_H = 100$ mV and the carbon content of the tungsten carbide catalysts

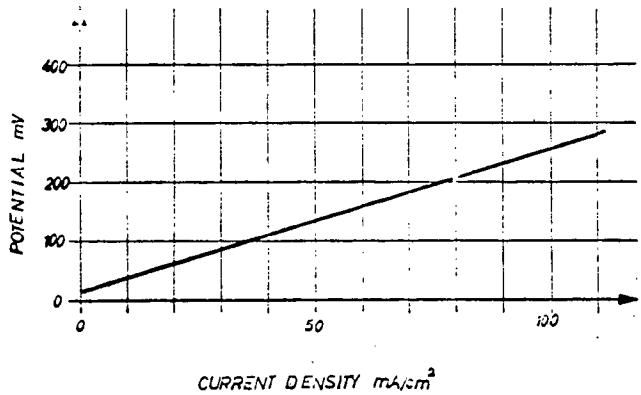

Fig. 9: Performance of a tungsten carbide anode with hydrogen