ON THE PERFORMANCE OF WC ELECTRODES UPON OXIDATION OF HYDROGEN, HYDRAZINE, AND FORMALDEHYDE

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1. Introduction

For wide application of fuel cells other than in space technology the one with an acid electrolyte will probably play the predominant part. We could show that in sulfuric acid hydrogen and carbon monoxide can be oxidized simultaneously at high current densities and temperatures below 100 °C at electrodes with pre-sulfurized platinum as the catalyst (1) (2).

However, the price of platinum, even if used in small amounts, is prohibitively high for the very broad application of fuel cells in everyday life. In the attempt to replace platinum a variety of substances has been investigated and proposed as a catalyst for a cell with an acid electrolyte. They did, however, not prove satisfactory. Some of them, e.g. $CoMoO_4$, are not even stable against the attack of sulfuric acid. The activity claimed for several other substances was presumably due to the presence of traces of platinum in the product used as the catalyst in a fuel-cell electrode. So far, we have only found tungsten carbide (WC) to be catalytically active, which has recently been described as a catalyst for the oxidation of hydrogen in acid electrolyte (3). The present paper deals with the preparation and the improvement of tungsten carbide electrodes at which not only hydrogen but also hydrazine and even organic substances can be anodically oxidized at considerably high current densities.

2. Preparation of Electrodes

Tungsten carbide which can serve as a catalyst has to be finely divided. Unfortunately, the commercially available substances generally do not meet this requirement. Tungsten carbide with a large surface area can be obtained, e.g., by precipitation from the gas phase or by the carburization of finely divided tungsten powder with carbonaceous gases (CO or CH_4). We pre-

pared the tungsten carbide required for our investigations by firing an intimate mixture of tungsten powder and soot at a temperature between 1100 °C and 1300 °C in a hydrogen atmosphere.

During the firing process sintering takes place and the resultant product can be used directly as an electrode provided that the starting mixture contained a pore-forming substance and was compressed to disks. Such an electrode is appropriate for the oxidation of fuels dissolved in the electrolyte or may even serve as a bubbling electrode for the oxidation of gaseous substances, such as hydrogen.

When using hydrogen as fuel, we usually prefer an electrode with polyethylene as a binder backed with a wet-proofing layer made from PTFE, as has been described elsewhere (4).

The best performance is achieved with electrodes containing a tungsten-carbide preparation whose carbon content is somewhat smaller than that corresponding to the stoichiometric value. An excess of carbon considerably decreases the catalytic activity of the product.

3. Electrochemical Measurements

3.1 Half-Cell Arrangement

For the electrochemical measurements we used the half-cell arrangement described in detail elsewhere (5), with an autogenous hydrogen electrode in the same electrolyte at the same temperature as the reference electrode. For use as a bubbling electrode the disks were fixed in a plexiglass ring by means of an adhesive and fitted in a specially designed electrode holder. Immersed electrodes were fixed by a tantalum wire loop. The electrolyte - 2N H_2SO_4 - was saturated with pure argon in order to exclude the influence of air. In most cases the measuring temperature was 70 °C.

3.2 Corrosion and its Effect on the Activity

In sulfuric acid free from oxygen corrosion of WC is negligibly small at open-circuit potential or even up to a potential of 300 mv. Between 300 and 500 mv a corrosion current is observed during periodic potentio-dynamic measurements (Fig. 1). After some sweeps this corrosion current starts to decrease and after some hours the corrosion has discontinued. While corrosion takes place the evolution of a gas is observed which means that part of the carbon contained in the carbide is oxidized to give carbon dioxide.

After cessation of corrosion, i.e., when the passive state is reached, the current density achieved with hydrogen is smaller than at the beginning of the experiment. Fig. 2 shows the decrease in activity for an electrode which has been corroded at a potential of 700 mv during 16 hrs. In this case the current density has decreased by about 20 per cent of the initial value.

It has never been observed that such a disactivated electrode can be reactivated by hydrogen gas applied to the electrode, not even at open-circuit potential; the inactive layer can be removed, however, by other means, e.g. by a treatment in potassium hydroxide solution.

A considerable increase in the activity instead of a disactivation is observed, however, when anodic corrosion takes place in the presence of a reducing agent, e.g., hydrogen bubbling through the electrode. Hence the activity of a WC electrode increases slowly during its operation as an anode for the oxidation of hydrogen. Such a slow increase in activity takes several days until a final state is reached where no further activation is observed. More defined results are obtained with a solution of hydrazine sulfate in the sulfuric acid electrolyte at a potential of about 600 to 700 mv maintained by means of a potentiostat. A period of some hours is sufficient to achieve optimum activity. In general the current density at a given potential can be increased up to twice its initial value.

Instead of hydrazine, formaldehyde dissolved in the electrolyte can be used as the reducing agent for the activation process. The reason why the application of a dissolved reducing agent is more effective than the application of hydrogen may be seen in the fact that a dissolved fuel can in any event reach those parts of the inner surface area of the electrode which are reached by the electrolyte, whereas in the case of hydrogen the pore-size distribution and the varying porosity may restrict the expected activation to only a small part of the inner surface area. An electrode which has been activated in the manner just described does not undergo further corrosion up to a potential of, say, 0.7 v, not even in the absence of any fuel.

Fig. 3 shows the current-potential plots obtained with an activated WC electrode under steady-state conditions upon hydrogen oxidation. At a potential of 300 mv and a temperature of 90 °C a current density of 160 ma/cm^2 is measured with this type of a sintered bubbling electrode. At a temperature of 25 °C the current density is reduced to 35 ma/cm^2. From the dependence of the current density on the temperature a mean value of 5.8 kcal/mole is derived for the activation energy at a potential of 300 mv.

A surprising observation is the fact that hydrazine is oxidized at a WC electrode at considerable densities, whereas it is not decomposed at open-circuit potential. Fig. 5 shows galvanostatic current-voltage plots obtained with hydrazine in 2N H_2SO_4 at a temperature of 70 °C. At a potential of 400 mv a current density of 80 ma/cm^2 is achieved under these conditions. Moreover, the figure clearly shows the influence of activation described above.

On the other hand, polarization is very high upon oxidation of hydrazine in sulfuric acid. The periodic potentiodynamic plot of Fig. 6 reveals that oxidation starts only at a potential of about 200 mv. This may be due to the fact that hydrazine sulfate is formed in the sulfuric-acid electrolyte so that a higher activation energy is required. Hence the performance of hydrazine on WC is somewhat improved by using a sulfuric-acid electrolyte with a concentration smaller than 2N, since in this case the solubility of hydrazine is greater. The best performance is achieved in a solution of hydrazine sulfate in water as the electrolyte.

Much more interesting than the oxidation of hydrazine appears the oxidation of formaldehyde. Fig. 7 shows that with formaldehyde a current density of about 60 ma/cm^2 can be achieved at a potential of 400 mv, and that the oxidation starts already at the potential of the hydrogen electrode.

The current density depends largely on the concentration of formaldehyde in the electrolyte, as is shown by Fig. 8.

Unfortunately, oxidation of formaldehyde nearly stops at the stage of formic acid, which is only slowly oxidized. At a potential of 200 mv and a temperature of 70 °C a current density as low as 1 ma/cm^2 is observed (Fig. 9). Even at 90 °C the oxidation rate is small compared with that of formaldehyde. An interesting feature in the oxidation of formic acid at 90 °C is the observation that it is dehydrogenated at the WC electrode under open-circuit conditions. At low current densities the oxidation of hydrogen evolved in the decomposition is the rate-determining step; at higher current densities the rate of dehydrogenation is insufficient, and direct oxidation of formic acid has to take place. This new process requires a higher potential. The maximum current density is reached at a potential of about 400 mv, as is shown by the peak in the periodic potentiodynamic current-voltage plot (Fig. 10).

Acetaldehyde, too, is oxidized at WC. Fig. 11 shows that a current density of about 20 ma/cm^2 is measured at a potential of 400 mv in periodic potentio-dynamic investigations. Under steady-state conditions the current density decreases to about 10 ma/cm^2 (Fig. 12). In the potential range considered, the oxidation stops completely at the stage of acetic acid. This means that at WC electrodes acetic acid can be formed from acetaldehyde in an electrochemical reaction, a process which might be of interest to the chemical industry.

With propionaldehyde only small current densities are observed, which are even smaller in the case of other aldehydes.

Neither alcohols, not even methanol, nor carboxylic acids other than formic acid can be electrochemically oxidized at WC electrodes in sulfuric acid.

4. Conclusions

Our investigations show that WC is an interesting new electrocatalyst at which not only hydrogen but also a variety of other substances can be oxidized. From our findings we conclude that the activation process described in this paper is due to the formation of tungsten oxides other than WO_3 with an oxidation number smaller than six, for instance tungsten bronzes of the type H_xWO_3, first reported by Glemser and Naumann (6). These bronzes are considered as activators of platinum catalysts in the oxidation of carbon monoxide (7). Thus it might be the combination of such a bronze with WC as the carrier which gives rise to the good performance observed. We hope that these results will help us in our efforts to replace platinum as a catalyst even for the direct electrochemical oxidation of methanol or hydrocarbons.

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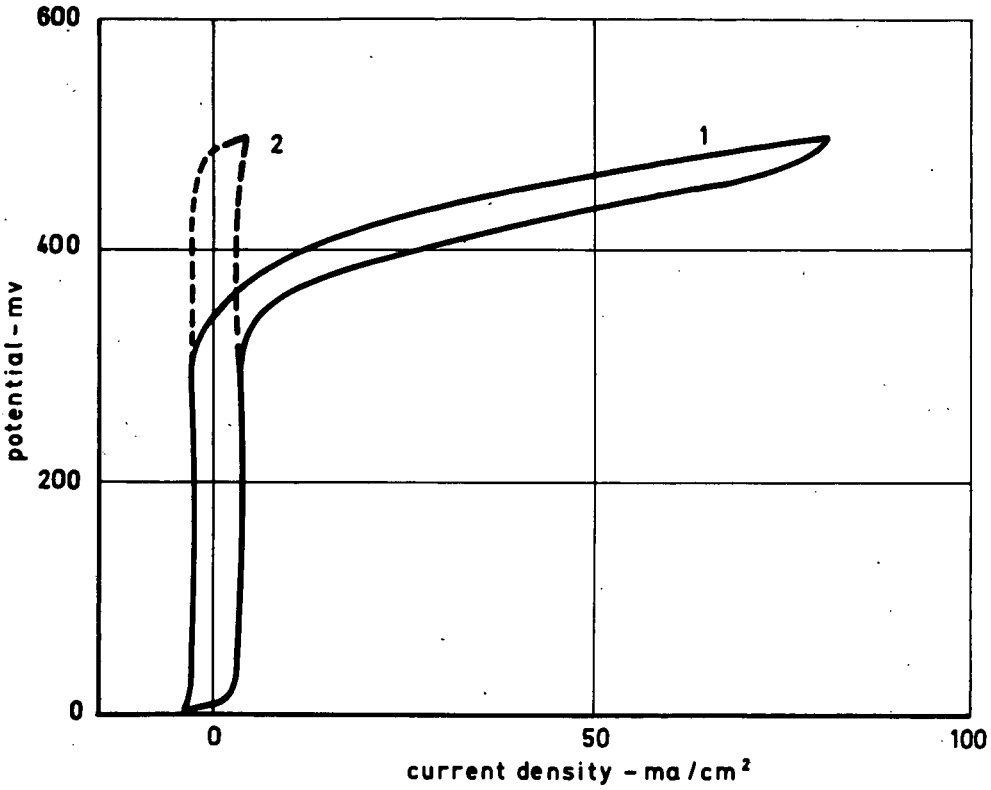

Fig. 1 Corrosion of WC in 2N H_2SO_4 at Anodic Potentials in the Absence of Reducing Agents at 70 °C. Periodic Potentiodynamic Current-Potential Plots; dU/dt = 40 mv/min.

Curve 1: Initial State
Curve 2: Final (Passive)State

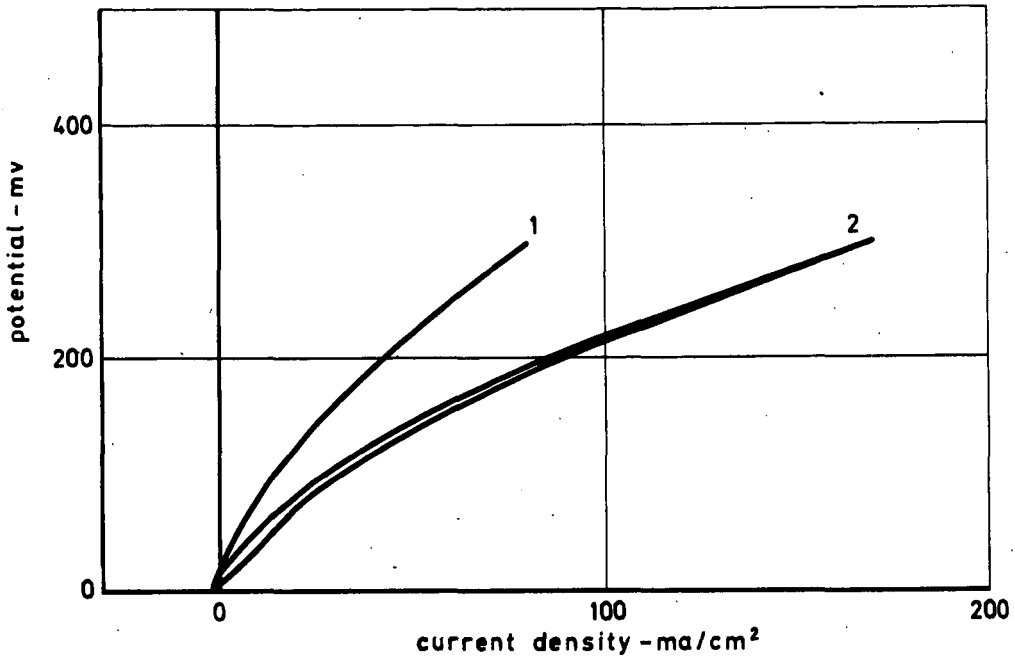

Fig. 2 Oxidation of Hydrogen at a WC Electrode in 2N H_2SO_4 at 70 °C. Periodic Potentiodynamic Current-Potential Plots; dU/dt = 100 mv/min.

Curve 1: Initial State
Curve 2: After Activation at a Potential of 650 mv in the Presence of Hydrogen

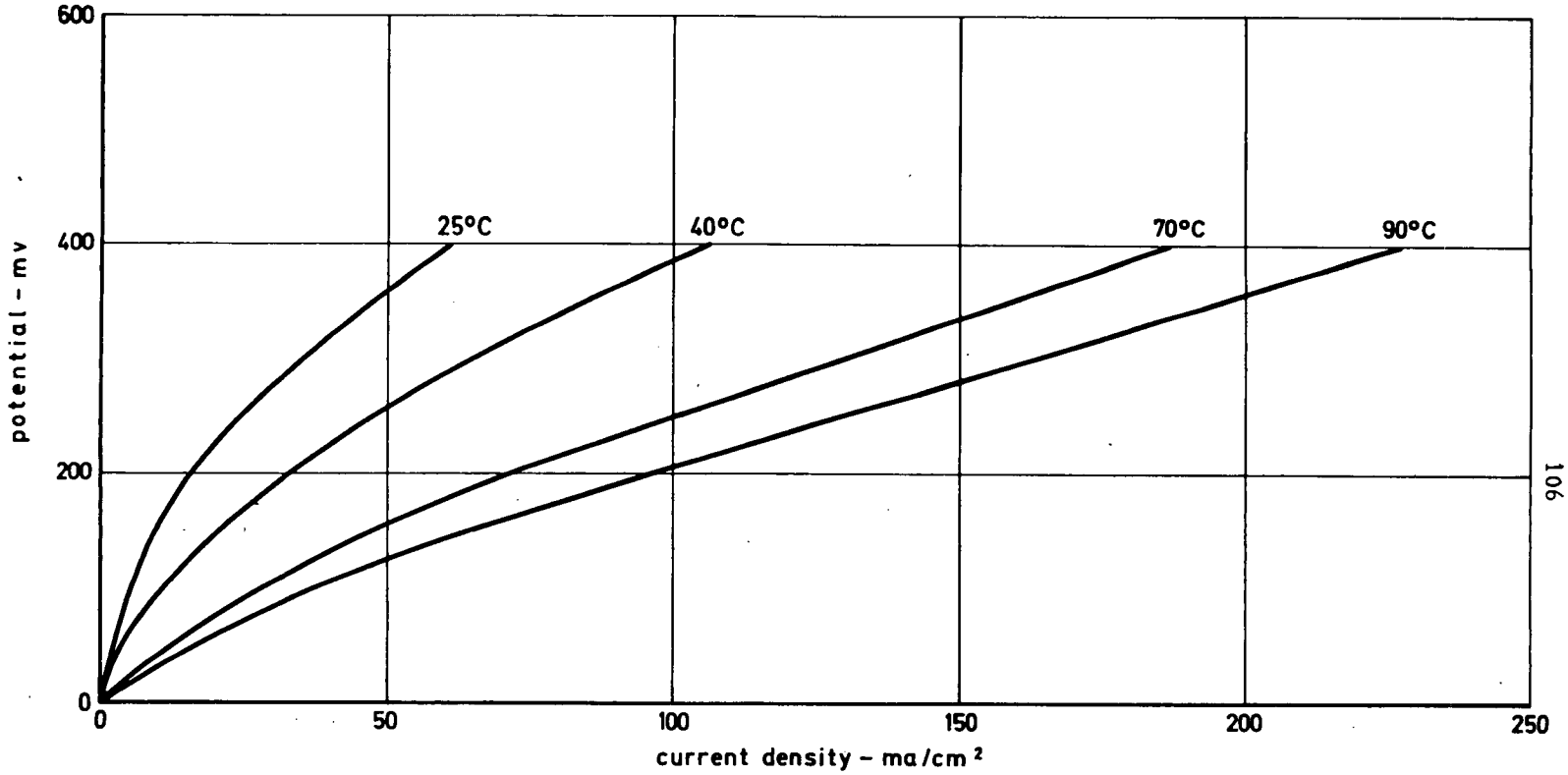

Fig. 3 Effect of Temperature on the Rate of Hydrogen Oxidation at a WC Electrode in 2N H_2SO_4 under Steady-State Conditions

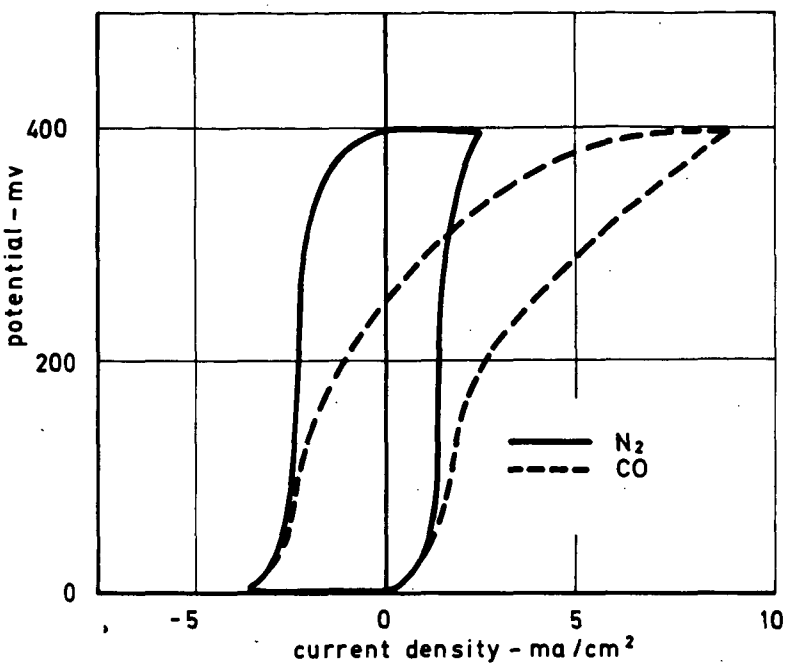

Fig. 4 Oxidation of Carbon Monoxide at a WC Electrode in 2N H_2SO_4 at 70 °C. Periodic Potentiodynamic Current-Potential Plots; dU/dt = 40 mv/min.

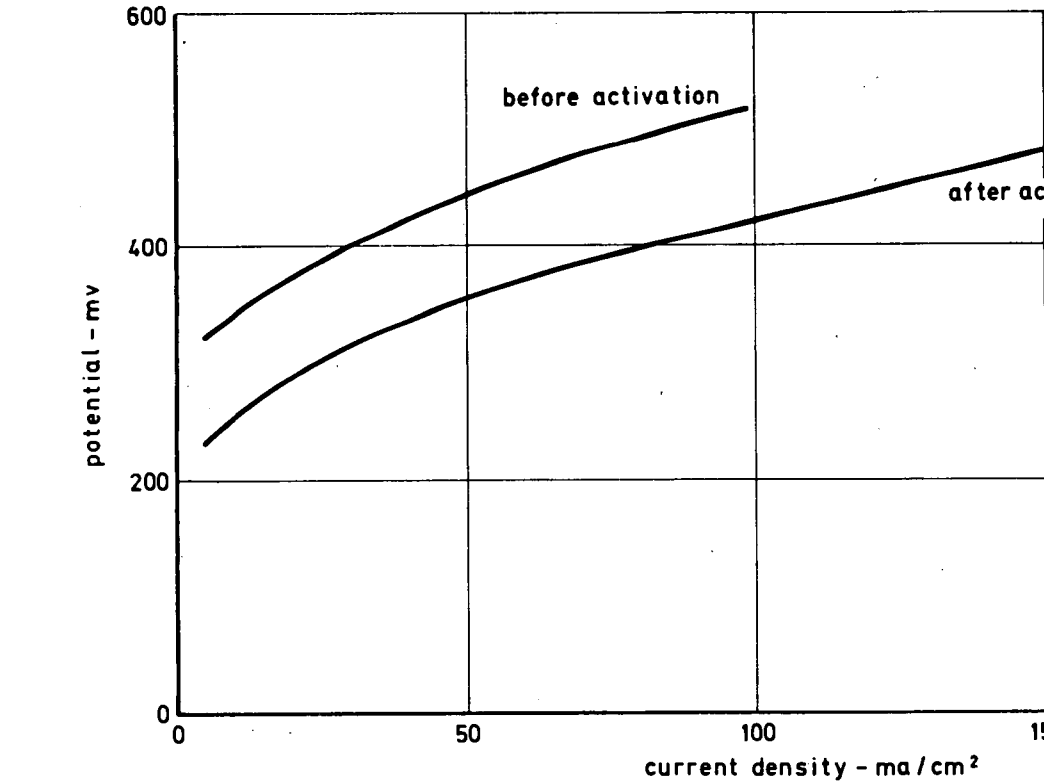

Fig. 5 Oxidation of Hydrazine at a WC Electrode in 2N H_2SO_4 at 70 °C under Steady-State Conditions

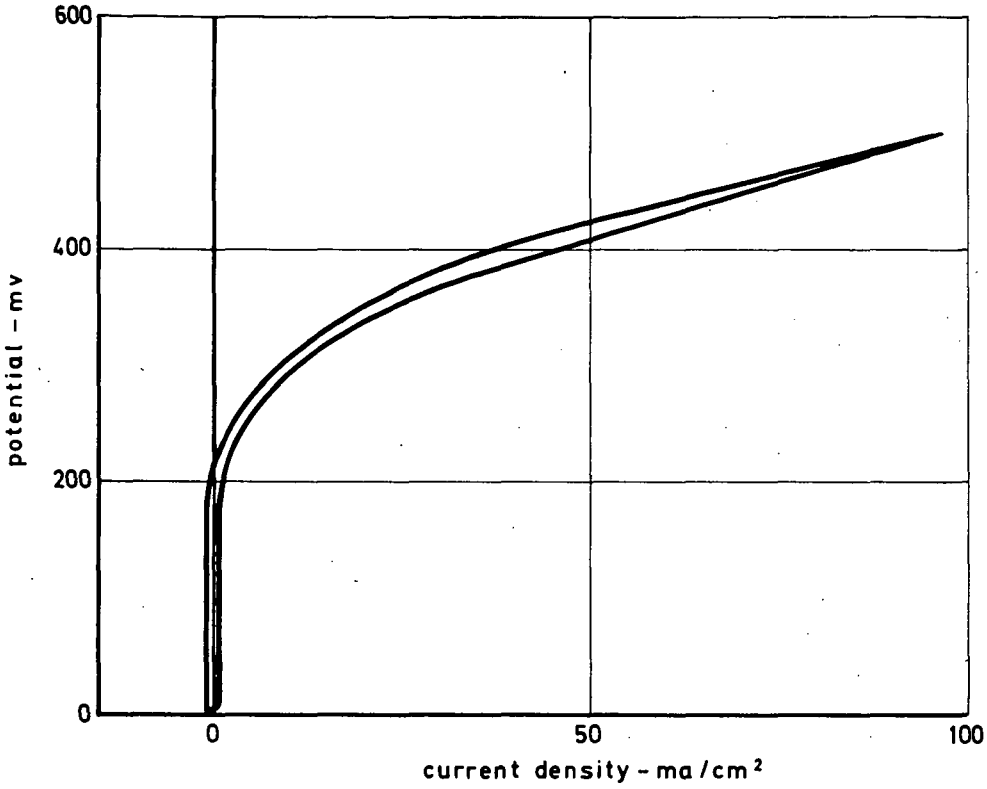

Fig. 6 Oxidation of Hydrazine at a WC Electrode in 2N H_2SO_4 at 70 °C. Periodic Potentiodynamic Current-Potential Plot; dU/dt = 100 mv/min

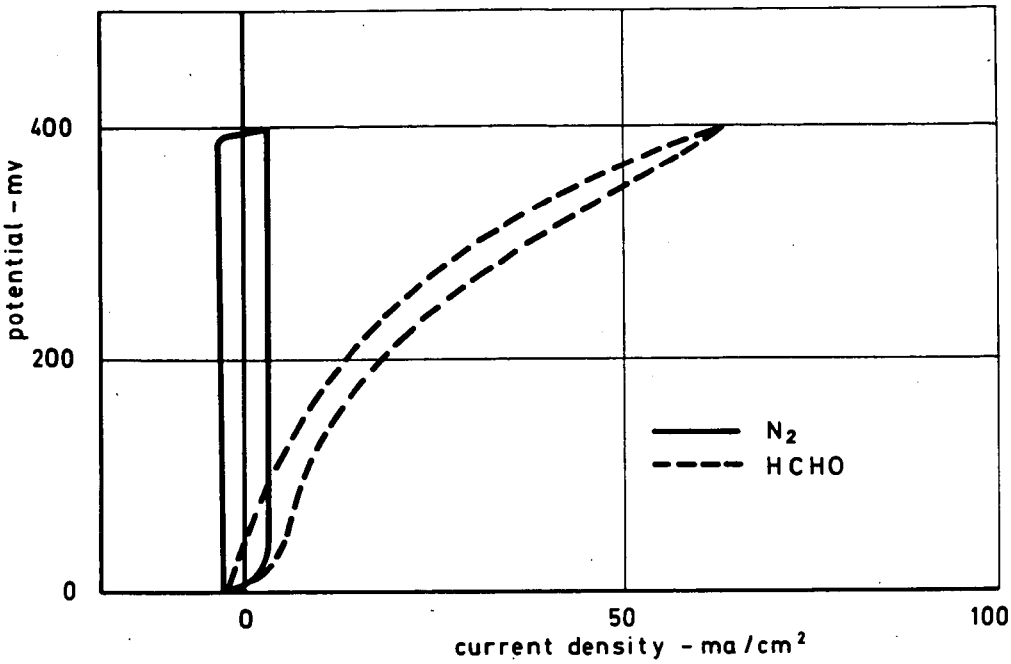

Fig. 7 Oxidation of Formaldehyde at a WC Electrode in 2N H_2SO_4 at 70 °C. Periodic Potentiodynamic Current-Potential Plot; dU/dt = 100 mv/min

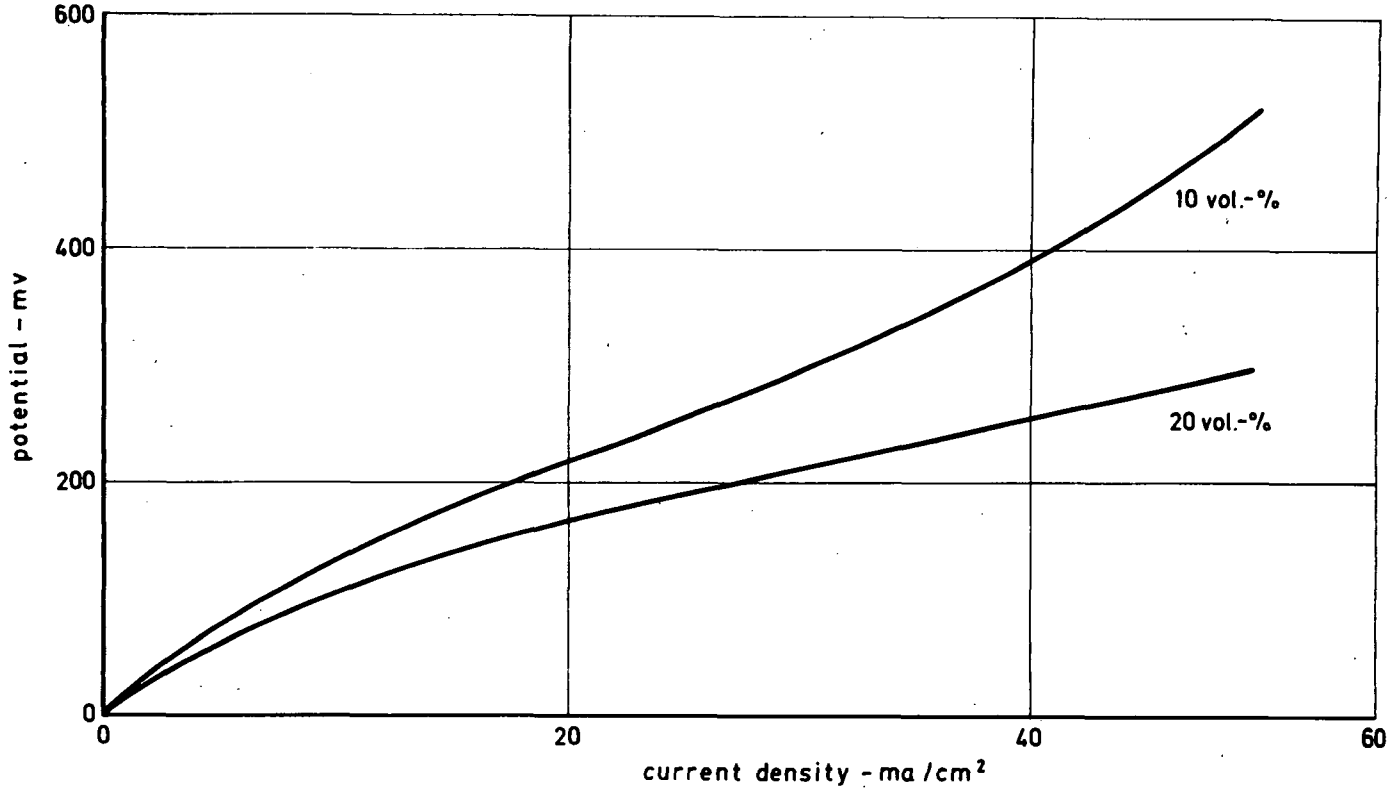

Fig. 8 Effect of Formaldehyde Concentration on the Performance of a WC Electrode in 2N H_2SO_4 at 70 °C under Steady-State Conditions

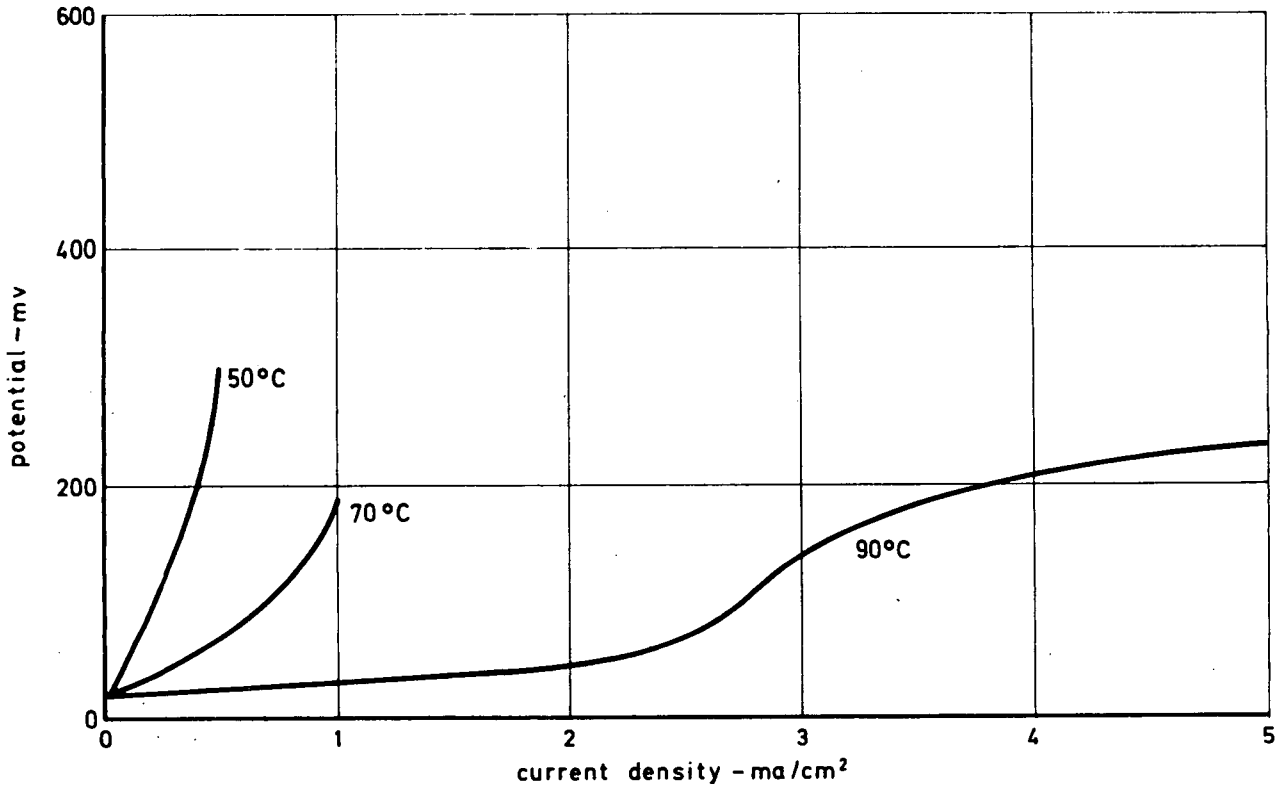

Fig. 9 Effect of Temperature on the Rate of Formic Acid Oxidation at a WC Electrode in 2N H_2SO_4 under Steady-State Conditions

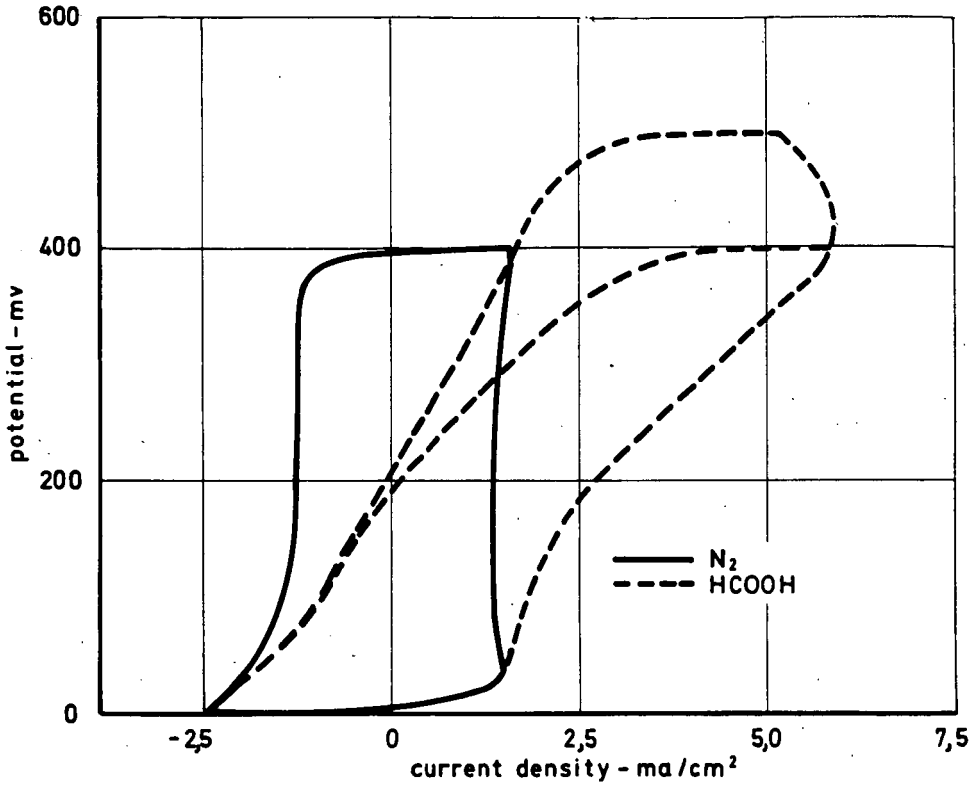

Fig. 10 Effect of an Intermediate from Formic Acid Oxidation on the Performance of a WC Electrode in 2N H_2SO_4 at 70 °C. Periodic Potentiodynamic Current-Potential Plots; dU/dt = 40 mv/min

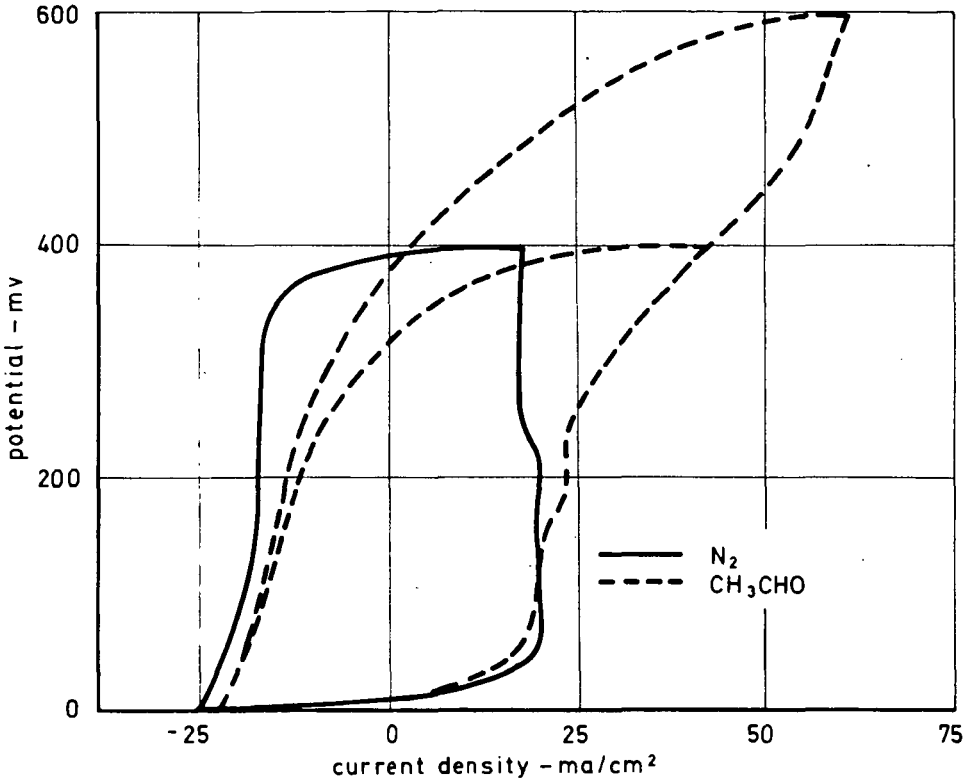

Fig. 11 Oxidation of Acetaldehyde at a WC Electrode in 2N H_2SO_4 at 70 °C. Periodic Potentiodynamic Current-Potential Plots; dU/dt = 100 mv/min

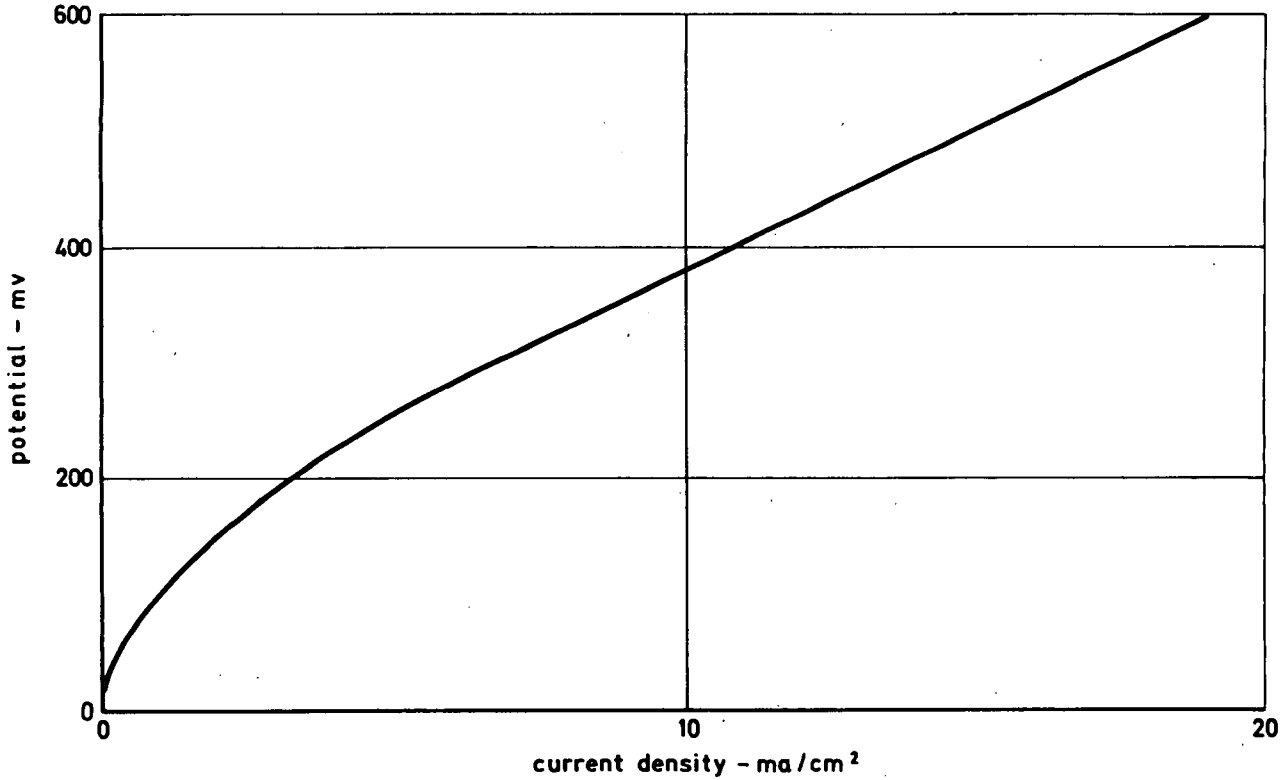

Fig. 12 Oxidation of Acetaldehyde at a WC Electrode in 2N H_2SO_4 at 70 °C under Steady-State Conditions