CORROSION RESISTANCE AND CATALYTIC ACTIVITY OF TUNGSTEN CARBIDE IN PHOSPHORIC ACID

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Summary

Studies of the corrosion and the catalytic activity of tungsten carbide, synthesized from the white modification of tungstic acid by carburization in CO at low temperature (700 °C) in phosphoric acid are reported. Oxidation of the surface and partial dissolution of the catalyst, as well as alterations of the specific surface and catalytic activity, were observed at 20 °C. Carbides with smaller initial specific surfaces were found to retain their catalytic activity for a longer period of time.

The corrosion rate of gas diffusion electrodes, catalysed with tungsten carbide was found to be substantial during operation at 150 °C and with current densities of 50 mA cm^{-2} in a hydrogen atmosphere. These electrodes displayed stable operation during the initial 200 - 220 h, but then their polarization increased. The possible reasons for such behaviour are discussed.

1. Introduction

The results from several investigations carried out during the '70s provide evidence that H_2/O_2 fuel cells using H_3PO_4 electrolyte and electrodes catalysed with minute amounts of platinum (*e.g.*, 0.5 - 0.6 mg cm^{-2}) may attain high specific power and can be used to solve some of the problems caused by the energy crisis [1 - 3]. Two of the basic shortcomings of these power sources are: the susceptibility of platinum to poisoning, and its recrystallization during operation. The use of alternative catalysts, which are more resistant to poisoning, make the use of crude hydrogen fuel possible. A successful development in this respect is a fuel cell which uses anodes catalysed with WC, synthesized from WO_3, developed at the laboratories of AEG–Telefunken. This fuel cell operates equally well both with pure hydrogen and with cracking gas [4], although the WC corroded during the initial 10 days, and then the process was complete. As a result, about 10% of the carbide was transferred into the solution [5].

Our investigation was aimed at:

(a) Checking the corrosion resistance of WC prepared from the white modification of H_2WO_4 under the operating conditions of a fuel cell with H_3PO_4 electrolyte.

(b) Collecting information to determine whether the double-layer gas diffusion hydrogen electrodes catalysed with these carbides were useful at elevated temperatures in H_3PO_4.

The experiments were carried out with two types of WC (WC-I and WC-II) having specific surface areas of 8 and 20 $m^2 g^{-1}$, respectively, and synthesized from the white modification of H_2WO_4 by carburization of CO at low temperature (700 °C). Prepared in this way, the carbon content in the WC lattice is substantially sub-stoichiometric, and the carbide displays excellent catalytic activity toward the hydrogen reaction in sulphuric acid [6]. It was for this reason that we chose to test tungsten carbide in phosphoric acid.

The corrosion resistance of the carbides was investigated under conditions simulating the operational regime of similar fuel cells. Hence, the catalyst was exposed to air at atmospheric pressure under open circuit conditions, rather than at a controlled potential, in the working electrolyte at 20 °C, and was operated in a hydrogen atmosphere at 150 °C in concentrated H_3PO_4 with a current density of 50 mA cm^{-2}.

The first stage of these investigations used powdered WC, as it allowed the possibility of acquiring more complete data concerning the changes that occur during corrosion. In the second stage, experiments were carried out with double layer gas diffusion electrodes. The active layer of the latter contained Teflonized active carbon in the optimum ratio as determined during the studies in sulphuric acid [7].

2. Experimental

2.1. Corrosion tests

(a) Powder samples

Five hundred milligram samples of powdered WC were placed in measuring flasks and concentrated H_3PO_4 was added. The samples were checked after 120, 220, 360, 500, 1000, 1500 and 2000 h by spinning, rinsing with distilled water until a pH of 7 was reached, and then drying at 120 °C to determine any change caused by corrosion.

The composition of the samples was determined by X-ray analysis but where tungsten oxides were detected they were chemically analysed to determine their bulk composition [8].

The specific surface area of all samples was determined by BET measurements. The changes in the morphology of the particles was checked by scanning electron microscopy (SEM).

Since information in the literature indicated that the corrosion products were soluble in phosphoric acid [5], their tungsten contents were determined by spectral analytical methods (inductively coupled plasma atomic emission spectrometry).

(b) Catalyst in gas diffusion electrodes

Tungsten carbide in the gas diffusion electrodes corrodes during operation at 150 °C and during stand-by (open circuit) periods at 20 °C. The samples were also checked at regular intervals during operation by X-ray measurements of the electrode, and spectral analysis of tungsten in the electrolyte.

2.2. Catalytic activity

(a) Powder samples

The electrochemical measurements of the powder samples were carried out with sedimented electrodes prepared by precipitating WC from an alcohol suspension at 20 °C onto a tantalum collector. The amount of WC varied between 0.5 and 1 mg to ensure the participation of the entire surface in the electrochemical process [9].

The catalytic activity for the hydrogen oxidation process was evaluated by plotting the voltage–current curves of the electrodes in phosphoric acid at 150 °C using a RADELKIS OH 150 potentiostat. Current densities were evaluated per unit of real surface area as determined by Brunauer–Emmet–Thaller measurements. The potentials were measured relative to a Giner hydrogen reference electrode immersed in the working electrolyte [10].

(b) Gas diffusion electrodes

Galvanostatic voltage–current curves were plotted in concentrated H_3PO_4 solutions at 150 °C, and long term tests were carried out at a current density of 50 mA cm^{-2}.

3. Results and discussion

Table 1 shows the changes which occur in both samples during immersion in phosphoric acid at 20 °C.

TABLE 1

Changes of tungsten carbides after different corrosion exposure times (τ) in conc. H_3PO_4 at 20 °C

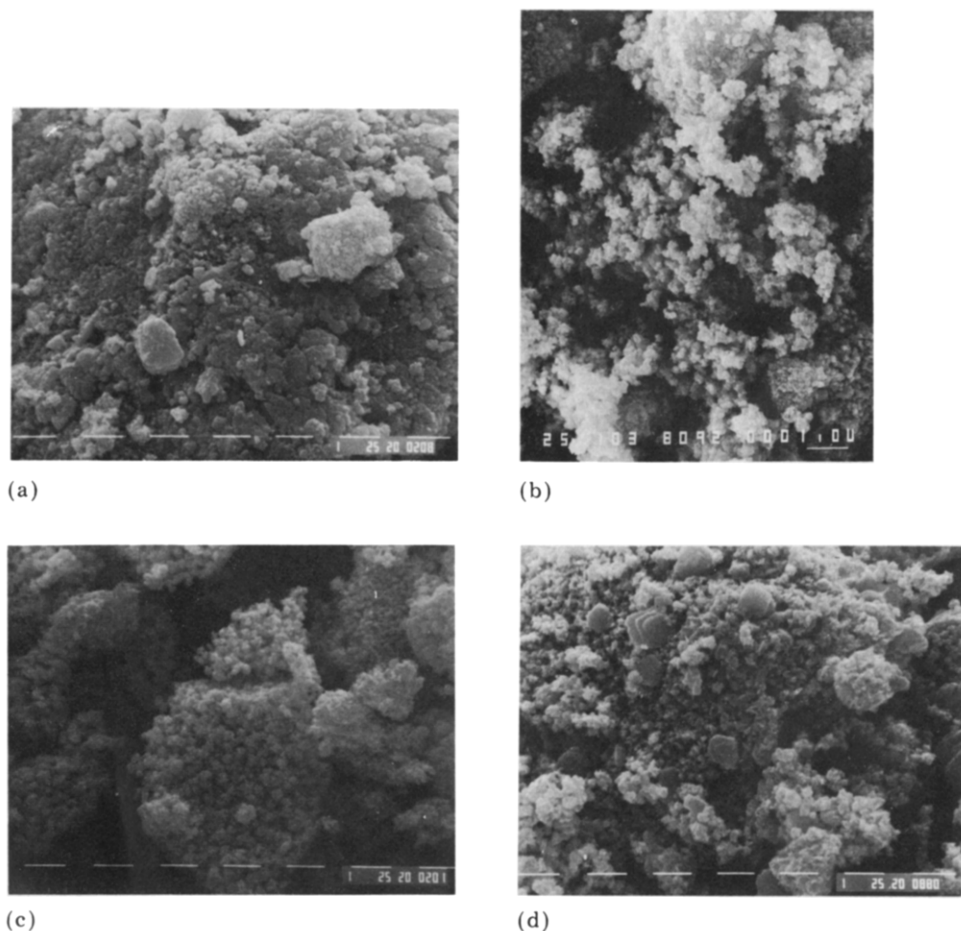| Hours	WC-I				WC-II			
	S (m^2 g^{-1})	WC losses (wt.%)			S (m^2 g^{-1})	WC losses (wt.%)		
		as WO$_2$	as W$_{dissolved}$	Total		as WO$_2$	as W$_{dissolved}$	Total
0	8.0	—	—	—	20.95	—	—	—
220	14.3	—	—	—	15.80	—	—	—
360	13.4	—	—	—	—	—	—	—
500	15.5	—	—	—	16.10	—	1.2	1.2
1000	22.5	—	—	—	11.2	3	3.5	6.5
1500	18.6	3	—	3	12.9	5	4.0	9.0
2000	12.1	6	7	13	—	—	—	—

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(a)

(b)

(c)

(d)

Fig. 1. Scanning electron micrographs of WC-I and WC-II after different exposure to corrosion (τ) (×10 000). WC-I: (a), 0 h; (b), 1000 h; (d), 2000 h. WC-II: (c), 0 h.

The "WC losses" are the weight percent. content of tungsten oxides on the surface of the samples, plus the weight percent. of tungsten dissolved in the electrolyte, calculated as WC.

Table 1 also shows that in H_3PO_4 the surface area of WC-I increases slowly to reach 22 m^2 g^{-1}. The micrographs in Fig. 1(a), (b) provide evidence that this is due to surface etching of the particles, and their disintegration into substantially finer grains. Carbides with surface areas of about 20 m^2 g^{-1} display a highly porous structure (Fig. 1(b), (c)) which enhances the corrosion process. As a result, a levelling of the particles begins, and the very fine-grained particles are completely dissolved (Fig. 1(d)). Data presented in Table 1 show that the corrosion of carbides with a large specific surface area results in a decrease of their surface and a dissolution of W in the electrolyte. After 1500 - 2000 h in contact with H_3PO_4, the losses in both samples are identical — approximately 10 - 12%. It must be mentioned, however, that

the corrosion rate of WC synthesized from the white modification of H_2WO_4 under identical conditions of temperature and time in a 20% H_2SO_4 solution is greater by a factor of two [8].

The analytical determinations described above were combined with investigations to determine how the catalytic activity of carbides varied when subjected to corrosion tests at room temperature.

Potentiostatic Tafel plots obtained in a hydrogen atmosphere at 150 °C were linear up to 100 mV.

Figure 2 shows the activity of the catalyst at 80 mV (to minimise the transport limitations) with the current determined only by the electrochemical activity of the carbide, as a function of time. It can be seen that the catalyst activity rises to a maximum of about 100 μA mg^{-1} after 1000 h immersion. It also shows that there is a slight increase in the specific catalyst activity for about 1000 h to approximately 0.45 μA cm^{-2}, but it then decreases until, at 2000 h, it is only half the initial value. The initial rise is probably due to the formation of surface oxides [11] while the decrease is probably due both to the accumulation of tungsten oxides on the surface and to the dissociation of the finer particles.

A proportional relationship between activity and specific surface area is also observed with WC-II samples, which display a decrease of the specific surface area, and, consequently, lowered activity, during the initial hours of the corrosion test.

Since WC-I retained its activity longer, the gas diffusion electrodes used in the following test runs were catalyzed with this type of material.

The alterations that occurred in the WC catalyst embodied in the active layer of the gas diffusion electrodes are presented in Table 2. The X-ray diffraction patterns showed that during operation in hydrogen for up to 350 h the electrode surface remained oxide-free. Spectral analysis data however
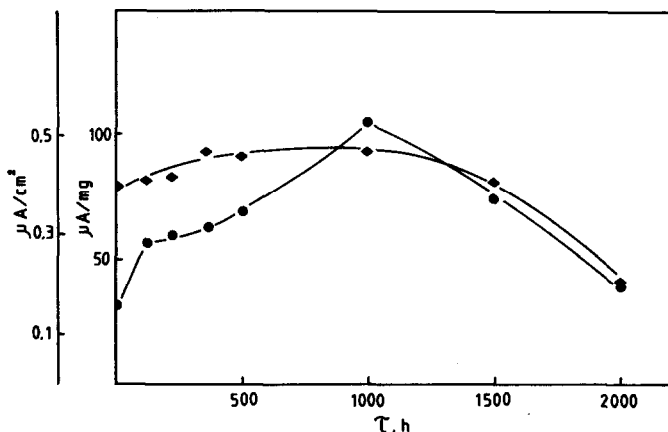

Fig. 2. Catalytic activity (μA mg^{-1} at φ = 80 mV), •; specific catalytic activity (μA cm^{-2} at φ = 80 mV), ◆; measured with sedimented WC electrodes after different duration of exposure to corrosion (τ) in concentrated H_3PO_4 at 150 °C.

TABLE 2

Changes of WC in the active layer of gas diffusion electrodes after different operation times (τ) in conc. H_3PO_4 at 150 °C and c.d. 50 mA cm^{-2}

Hours	WC losses (wt.%) ($W_{dissolved}$)
10	2.5
16	3.0
43	4.2
100	8.0
250	17.5
350	25.0

provided evidence that dissolved tungsten was present in the electrolyte even after the initial 10 h of operation. After 350 h, approximately 25% of the tungsten content of the carbide catalyst incorporated in the gas diffusion electrode was dissolved in the electrolyte.

Dissolution can be substantially accelerated if the hydrogen flow is interrupted. In this case, the potential increases to 600 - 650 mV (HE), and after only two hours 70% of the WC is dissolved.

These results proved that WC synthesized from H_2WO_4 has an acceptable corrosion resistance in H_3PO_4 at 20 °C, but is not stable under the operational conditions of phosphoric acid fuel cells.

The behaviour of the electrodes was investigated further in an effort to evaluate completely the possibilities of the use of these carbides as catalysts.

The initial voltage–current curves of the gas diffusion electrodes were rather modest but they improved with time, as shown in Fig. 3. The difference between the potential under open circuit conditions from the hydrogen equilibrium potential is likely to be related to corrosion associated with enriched oxygen dissolved in the electrolyte. Optimum performance is reached after approximately 80 operational hours. This may result not only from an enhanced catalytic activity due to increased surface area, but also from the slow penetration of phosphoric acid into the pores of the active layer until complete wetting is reached.

The following experiment was carried out to try to establish whether wetting can improve the characteristics of the electrodes. The electrode was fixed in the half-cell and kept in contact with the electrolyte for 80 h. The resulting voltage–current curve (Fig. 3) demonstrated that the penetration of H_3PO_4 into the pores of the active layer plays an important role in the performance of the electrode. Similar phenomena were observed during the long term tests of oxygen gas diffusion electrodes operating in concentrated H_3PO_4 electrolytes [10].

The electrode performance can be improved by altering the active layer thickness but retaining the ratio between the components, as shown in Fig. 4. In Fig. 5 it is shown how the activity of the electrode can also be enhanced by operating at elevated temperature.
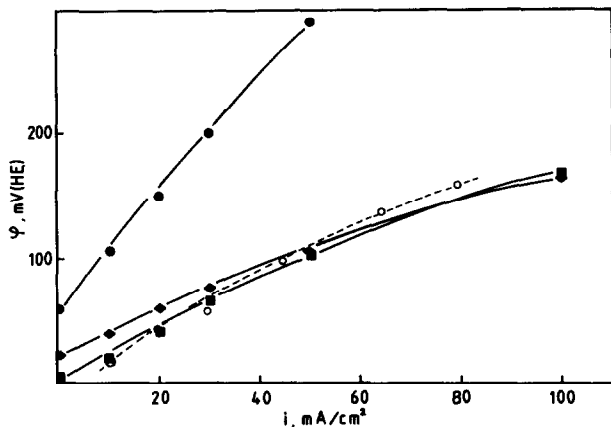
Fig. 3. Voltage–current curves of gas diffusion electrodes (40 mg WC cm^{-2}) in concentrated H$_3$PO$_4$ at 150 °C using WC-I. ●, initial; ◆, after 80 h operation at a c.d. of 50 mA cm^{-2}; ■, after 100 h operation at a c.d. of 50 mA cm^{-2}; ○, after 80 h contact with the electrolyte.
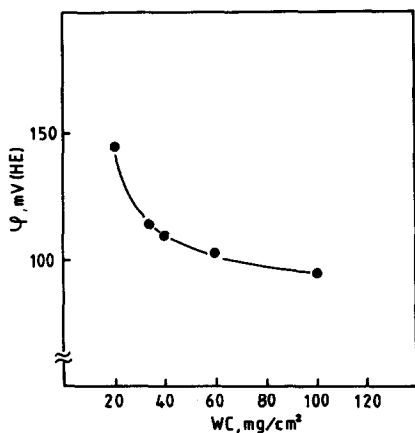

Fig. 4. Polarization vs. amount of catalyst in the gas diffusion electrode at a c.d. of 50 mA cm^{-2} in conc. H$_3$PO$_4$ at 150 °C using WC-I.
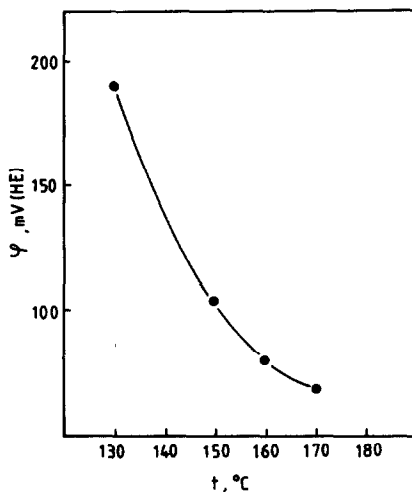
Fig. 5. Polarization of the gas diffusion electrode (40 mg WC cm^{-2}) vs. temperature at a c.d. of 50 mA cm^{-2} in conc. H$_3$PO$_4$ using WC-I.

The long term tests of these electrodes provide evidence that, after reaching the optimal characteristics, they can operate stably for between 200 and 220 h. Polarization then increases to higher values, as shown in Fig. 6. An estimate of the corrosion current which flows during the long term test has shown that its value is only about 0.02% and, therefore, it does not affect the initial electrode characteristics. The increased polarization with time, however, probably results from the partial dissolution of the catalyst.
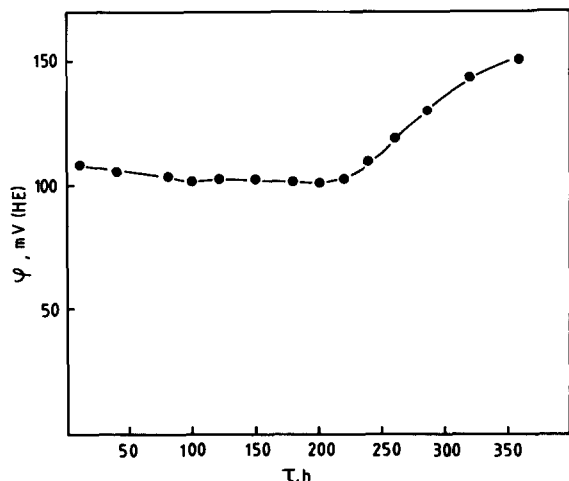
Fig. 6. Long term tests of a gas diffusion electrode (40 mg WC cm^{-2}) at a c.d. of 50 mA cm^{-2} in conc. H_3PO_4 at 150 °C using WC-I.

4. Conclusion

These investigations lead one to conclude that WC catalysts, synthesized from white H_2WO_4 display good activity in concentrated H_3PO_4 but poor corrosion resistivity at elevated temperatures. This shortcoming could be due to the lower than stoichiometric carbon content, i.e., to the greater number of defects in the crystal lattice. For this reason it is concluded that the tungsten carbide which was studied is not a suitable catalyst for the oxidation of hydrogen in phosphoric acid.

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