

INFLUENCE OF BONDING AND FILLING AGENTS ON THE ACTIVITY OF TUNGSTEN CARBIDE HYDROGEN ELECTRODES

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(Received June 14, 1976; in revised form October 11, 1976)

Summary

The structure of polytetrafluoroethylene and polyethylene bonded tungsten carbide electrodes was varied by changing the ratio of the bonding agent to the catalyst, and by adding various amounts of fillers of a different type. Of the series of fillers used, good results were obtained with oxalic acid, ammonium chloride and ammonium nitrate. The effect of the filler was ascribed to its influence on the surface properties of the pore wall rather than to the rise in the porosity of the electrode.

Introduction

Since 1968 when the first results on the anodic oxidation of hydrogen on tungsten carbide electrodes were presented by Pohl and Böhm [1] in Brussels, tungsten carbide has received increased attention as an electro-catalyst for fuel cells operating with an acid electrolyte. At present, it is the best non-noble catalyst in the field. Its efficiency is comparable to platinum, and it is superior to platinum as far as catalyst poisoning is concerned. A further advantage of tungsten carbide rests in its availability and low cost (as compared to platinum group metals).

The activity of a tungsten carbide catalyst is highly dependent on the mode of its preparation [2], especially on the temperature and time of carburization and on the composition of the gas mixture used. In 1972, Svatá *et al.* [3] and later Hung *et al.* [4] independently worked out methods for preparing active WC catalysts by reducing and carburating tungstic oxide or acid with hydrogen and carbon monoxide. From the catalyst, electrodes were prepared for testing the catalytic activity but no special attention was paid to the structure of the electrodes owing to the fact that with the

changes in the conditions of the preparation of the catalyst, the samples differed greatly in both grain size and activity. Only after a satisfactory activity had been obtained, was attention aimed at the structure of the electrodes in order to obtain thin lightweight electrodes with a stabilized position of the three-phase boundary, capable of long operating life without overpressure, and permitting low catalyst loadings to be employed. The results of this endeavour are the subject of the present paper.

Experimental

A series of electrodes was made from tungsten carbide (WC) samples prepared by processes described before [3 - 5]. In composition, the samples were all basically WC differing in purity, grain size and structure, and surface area. The catalysts were bonded with polytetrafluoroethylene (PTFE, Hostaflon TF 16, Hoechst, Germany) or polyethylene (PE, Hostalen GUR, Hoechst, Germany) powders. To increase the pore volume, a series of filling agents was used: $(\text{COOH})_2$, $(\text{NH}_4\text{COO})_2$, KHCO_3 , NH_4HCO_3 , NH_4NO_3 , NH_4Cl , KCl , Na_2SO_4 , all A.R. grade. The filling agents were classified on sieves to yield a fraction in the size range 40 - 60 μm . The catalyst and the bonding and filling agents were mixed in a high-speed mixer, and pressed in a 31 mm diameter die at a pressure of 1 t/cm².

The compacts obtained were then sintered in an inert atmosphere for 70 min at 300 and 150 °C for PTFE and PE electrodes respectively. Fillers which do not decompose during sintering were washed out with distilled water, and the electrodes were dried again at 105 °C. Quantitative removal of the filler was controlled by weighing. Unless stated otherwise, the quantities of the catalyst, PTFE(PE), and filler were 2.5, 0.5(0.24), and 0.2 g. Double-layer electrodes were also prepared; one layer intended as a gas layer was rich in the bonding agent, the other, an electrolyte layer, had only the lowest quantity of the agent required for mechanical strength. The weight ratios of WC, PTFE(PE) and filler were 1.25, 0.4(0.24), 0.1 and 1.25, 0.1 (0.06) and 0.1 for the gas and electrolyte layers respectively. The activity of the electrodes was compared by measuring, in a galvanostatic regime, the current density obtained during oxidation of hydrogen in 1 N sulphuric acid at 60 °C in a half-cell arrangement described previously [6]. The current densities given in the Tables are referred to 1 cm² of the exposed surface area of the electrodes and a potential of 350 mV (standard hydrogen scale). Unless stated otherwise, the loading of the catalyst was 330 mg/cm². The reproducibility of the results was also determined. For two pairs of electrodes prepared by one procedure from one catalyst at one time, the current densities obtained were 108 and 108, and 102 and 108 mA/cm². For electrodes prepared from one catalyst at different times, the current densities were 108, 98 and 114, or in another case, 130, 140, 134 and 135 mA/cm². The reproducibility being satisfactory, only one series of electrodes was prepared for determining one dependence. If a smooth dependence was obtained, the

results were accepted as such otherwise additional measurements were made to confirm the values for the series.

Imbibition capacities of one-layer electrodes were measured. Pre-dried electrodes were immersed in distilled water where they were left for 24 hours. No vacuum was applied, in order to bring the conditions of saturation close to those in electrochemical measurements. Since, at first, the results were poorly reproducible due to unequal quantities of surplus water remaining on the electrode after superficial drying, drying was then performed by placing the electrodes into a stream of air saturated with water vapour by passing it through a set of Drechsel bottles. The values of pore volumes filled with water were compared to total porosities obtained from the difference between the true and apparent densities of the electrodes. The apparent density was calculated from the weight and volume, the true density was determined pycnometrically in an inert organic solvent.

Results and Discussion

Our first endeavour consisted in optimizing the ratio of the catalyst to the bonding agent. The results are given in Tables 1 and 2 for PTFE and PE, respectively. For a less active catalyst and for short duration measurements, there is no marked difference between the bonding agents and even the changes in their concentrations are not very important; for the more active catalyst 202, however, the dependence of the activity on the quantity of the bonding

TABLE 1

Dependence of current density (mA/cm^2) on the ratio PTFE/WC in single-layer electrodes

	g of PTFE per 2.5 g catalyst		
	0.6	0.3	0.2
202 S 4	99	49	34
SWC 03,08	36	43	42

TABLE 2

Dependence of current density (mA/cm^2) on the ratio PE/WC in single-layer electrodes

	g of PE per 2.5 g catalyst					
	0.48	0.36	0.30	0.24	0.18	0.12
202 S3		65	77	132	86	33
SWC 03,08	34	35	33	33	36	29

TABLE 3

Dependence of current density (mA/cm^2) on the loading of the catalyst in single-layer electrodes bonded with PE

	Catalyst loading (g/cm^2)		
	265	330	397
202 S3, 10% PE	70	86	102
SWC 03,08, 7% PE	32	35	40

TABLE 4

Dependence of current density (mA/cm^2) on the quantity of filling agent in single-layer electrodes

	g of $(\text{COOH})_2$ per 2.5 g WC 202 S3				
	0	0.1	0.2	0.4	0.8
0.24 g PE	132	85	80	*	*
0.50 g PTFE	50	183		180	

*Electrode potential kept increasing when on load.

agent is pronounced. We believe that the difference in the sensitivity of the two catalysts to the changes in the quantity of the bonding agent is due to the differences in their grain size. Catalyst SWC 03,08 is coarse-grained, about the same size as that of PTFE and PE powders. Thus the size of intergranular voids does not depend on the ratio of the two components. Catalyst 202, on the contrary, is extremely fine-grained and voluminous, the particles of the bonding agent being larger by two orders of magnitude than those of the catalyst. As a consequence, changes in the ratio of the two components manifest themselves not only in the wettability but also in the size of the pores in the resulting porous system. Thus for optimum operation, two requirements have to be met instead of one.

In all cases, electrodes bonded with PE were easily penetrated by the electrolyte, soon weeping on the gas side, especially in the case of an interruption in the gas supply. After renewal of the gas supply, the flooding was found to be irreversible in contrast to an electrode bonded with PTFE which recovered in a couple of hours. It is also apparent from Table 3 that electrodes bonded with PE work to a greater depth than those bonded with PTFE, as has already been observed [7]. It may be seen that the electrode performance increases with an increase in the loading of the catalyst (and the electrode thickness since they were pressed in one and the same die) — a fact which has not been observed with PTFE bonded electrodes. (By raising the loading of the catalyst by 100%, only a 15% rise in the current density was obtained.)

TABLE 5

Dependence of current density (mA/cm^2) of the filling agent species in single- and double-layer electrodes

Filler	PTFE-bonded electrodes					PE-bonded electrodes	
	Single-layer	Double-layer electrodes					
Catalyst:	Ws	202 S3	226	SWC 03,08	165 S	202 S3	SWC 03,08
None	*	91	82	*	51	98	33
$(\text{COONH}_4)_2$	16	106		36	68	59	33
$(\text{COOH})_2$	43	130	81	46		89	40
Na_2SO_4	33	54	65	*			38
KHCO_3	43	94		30		97	
KCl	*	64	70	*			
NH_4Cl	39	134					
NH_4NO_3	44	130					
NH_4HCO_3	18	88					
$\text{Na}_2\text{SO}_4, (\text{COOH})_2$	51	123					
$(\text{COOH})_2, \text{Na}_2\text{SO}_4$		113					
$(\text{COOH})_2, \text{KCl}$	49	97					
$\text{NH}_4\text{Cl}, \text{Na}_2\text{SO}_4$	50						
$\text{KCl}, \text{NH}_4\text{Cl}$	56						

*Potential kept increasing when on load.

The fact that the dependence of current density on catalyst loading is not linear is a consequence of the increase in the IR drop accompanying the growing electrode thickness; the current densities thus fall slightly.

The different response of electrodes bonded with PTFE and PE to the quantity of oxalic acid used as filler (Table 4) is interesting. PE bonded electrodes show a pronounced decrease in activity as the quantity of the filler increases. The decrease in the performance accompanying the increase in the filler volume is due to flooding, though, at the beginning of the experiment, gas bubbled through into the electrolyte. Contrary to this effect, in PTFE bonded electrodes the quantity of the filler used seems to be of no importance. An unfilled electrode does possess a low activity but no change of activity was observed in electrodes with a fourfold difference in the filler weight. This suggests that the promoting effect of the filler in these electrodes rests elsewhere than just increasing the pore volume.

Double-layer electrodes were prepared to ensure a fixed position of the three-phase boundary for long working life. Since there was a big difference in water repellency of the two electrode layers, the boundary was quickly established at the site of contact of the two layers, and the electrodes were capable of operation for several thousands of hours. The porosity of the electrodes was increased by using a variety of filling agents. The effect of the filler on the activity of the electrodes leaves room for argument (Table 5). In double layer electrodes bonded with PE, the differences between electrodes with and without fillers and similarly between electrodes with different

TABLE 6

Imbibition capacity of PTFE-bonded electrodes with various filling agents

Filler	Total pore volume (cm^3)	Pore volume filled with water	
		cm^3	%
None	0.23	0.24	100
$(\text{COONH}_4)_2$	0.38	0.27	71
$(\text{COOH})_2$	0.36	0.23	64
Na_2SO_4	0.40	0.26	65
KHCO_3	0.37	0.32	86
KCl	0.34	0.26	77
NH_4Cl	0.37	0.24	65
NH_4NO_3	0.36	0.28	78
NH_4HCO_3	0.34	0.29	85

Values in column 2 are averages of 6 measurements.

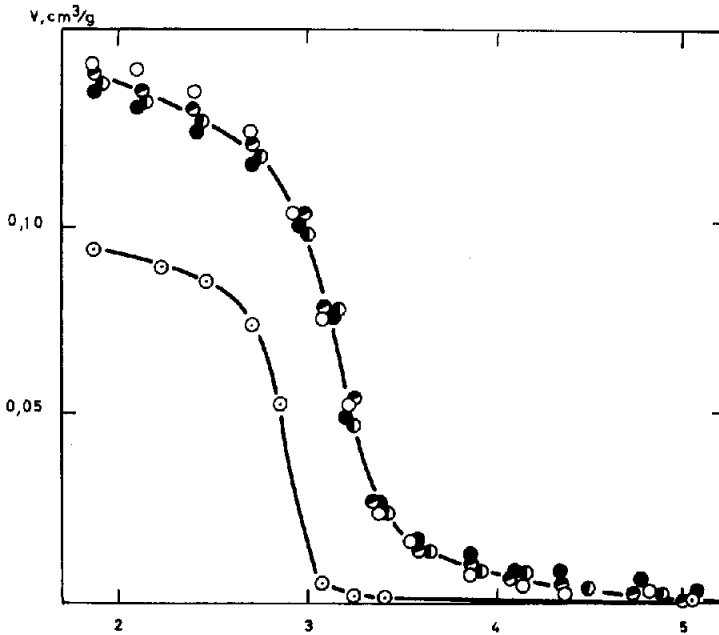


Fig. 1. Porosimetric curves of WC electrodes. \circ , unfilled; filled with: \circ , $(\text{NH}_4\text{COO})_2$; \bullet , KCl ; \bullet , $(\text{COOH})_2$; \bullet , Na_2SO_4 .

fillers are rather insignificant. Contrary to that, in electrodes bonded with PTFE the differences in activities are very marked; in the less active carbides (SWC 03,08, Ws), the presence of a filler is necessary for the electrode to be

capable of operation, in the more active catalysts the filler only promotes the performance. In the latter electrodes, the filler species is of great importance; some fillers improve the performance, others are detrimental. As already mentioned, this effect does not result from a change in the electrode structure. It is evident from Fig. 1, depicting porosimetric curves of some of the electrodes, that electrodes containing different fillers have practically identical structures. This is only natural since in all cases the filler was of the same size differing only in particle shape. It follows also from comparing the performances of filled and unfilled electrodes that the activity does not depend on the porosity, an unfilled electrode has a different size and quantity of pores but all the same its performance may be practically the same as that of a filled one. The possibility of a poisoning of the catalyst by some of the fillers is not probable either. On the one hand, one can hardly expect KCl for instance to be a poison when either of its ions when in combination with another partner, is favourable (NH_4Cl , KHCO_3). Besides, the poisoning would have to become apparent irrespective of the bonding agent which is not the case (compare cols. 1 and 7). There now remains the explanation that the filler forms a film on the pore walls which influences the wettability of the pore. This idea is supported by two facts: (1) the weeping effect exhibited by some of the electrodes. Electrodes filled with, for instance, NH_4Cl or NH_4NO_3 were wet through at the end of the measurement of the polarization curve whereas those filled with *e.g.* NH_4HCO_3 had their gas sides completely dry; (2) electrodes bonded with PE which are easily penetrated by the electrolyte are less responsive to the filler species than those bonded with PTFE (compare cols. 2, 4, 6, 7). Also, by comparing the current densities of catalyst 202 in Tables 2 and 5 (col. 2), it is evident that the same effect may be brought about by different means.

To verify the wettability assumption, imbibition capacities of the electrodes were measured. The data are brought together in Table 6. Column 1 gives the total pore volume as calculated from the densities, column 2 gives the volume of pores filled with water in cm^3 , and column 3 the same quantity in percentage of the total pore volume. It is apparent that there are differences in the quantity of water retained by individual electrodes but no correlation between the imbibition capacity and the activity of the electrode was found. Since, however, the imbibition capacity measured under the above conditions does not depict correctly the situation in a working electrode, a further attempt at verification of the wettability concept was made. Electrodes with a low performance were washed, dried, and impregnated with saturated solutions of filling agents which gave the best results and *vice versa*. It was found that by treating a "bad" electrode with a "good" filler the results improved markedly whereas "good" electrodes treated with a "bad" filler remained without major damage. This again confirms that there are changes in the surface properties of the pore wall, only the effect is rather complex, and will require further study.

References

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