

## Activity and corrosion of tungsten carbide recombination electrodes during lead/acid battery operation

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### Abstract

The oxidation of the tungsten carbide (WC) catalyst in recombination electrodes partially immersed in  $\text{H}_2\text{SO}_4$  solution was investigated when the electrodes operated in an atmosphere of oxygen and hydrogen. It has been established that after a long operation period (4000 h) 60 to 70% of the catalysts, depending on the initial active surface of WC, may be oxidized to  $\text{WO}_x$ , whereby the rate of recombination decreases about three times. It is assumed that the oxidation of WC is due to the  $\text{H}_2\text{O}_2$  formed as an intermediate product of the recombination of hydrogen and oxygen. Silver accelerates the decomposition of  $\text{H}_2\text{O}_2$  and hence the use of a WC–Ag mixture as catalyst in the recombination electrodes reduces strongly the carbide corrosion.

### Introduction

Tungsten carbide (WC) has long been known as being a good catalyst for hydrogen oxidation in acidic medium [1]. The results from recently performed investigations in our laboratory have shown that WC possesses a similar catalytic activity also with respect to the reduction of oxygen [2]. Based on these results a device has been developed for recombination of hydrogen and oxygen evolved during lead/acid battery operation [3]. The electrodes of this device can be catalyzed with WC alone or in combination with activated carbon. The latter is added to accelerate the oxygen reaction. This could result in an increase by 15 to 20% of the initial catalytic activity of WC electrodes with respect to the recombination of hydrogen and oxygen in the gas mixture. There are no data available in the literature, however, on the corrosion resistance of WC under the operating conditions of the lead/acid battery. WC corrosion, in this case, means oxidation of WC by the oxygen evolved, and the resulting formation of tungsten oxides ( $\text{WC} \rightarrow \text{WO}_x$ ). As reported earlier [4], the corrosion resistance of WC in a medium of  $\text{H}_2\text{SO}_4$  solution and air depends on the following factors: (i) type of raw material used for WC synthesis; (ii) WC specific surface, and (iii)  $\text{H}_2\text{SO}_4$  concentration.

Under identical test conditions, carbides synthesized from tungsten oxides corrode more slowly than those obtained from tungstic acid. When prepared from the same raw material, the corrosion resistance of WC is determined mainly by its specific

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surface, i.e., the larger the surface the lower the corrosion resistance of the carbide.

With increasing the concentration of  $H_2SO_4$ , the corrosion resistance of WC grows. It has been also established that carbide corrosion under the above conditions affects considerably its catalytic activity with respect to hydrogen oxidation [5].

Stationary lead/acid batteries operate under conditions of float charge with hydrogen and oxygen being continuously evolved in a stoichiometric ratio. If such batteries are equipped with partially immersed WC recombination electrodes, the latter will operate in a medium of oxygen and hydrogen and have to exhibit a sufficiently high catalytic activity during the whole service life of the batteries. One of the factors that reduce this catalytic activity is the corrosion of the WC catalyst.

The aims of the present paper are: (i) to determine the corrosion resistance of WC and the variations in its catalytic activity in an atmosphere of stoichiometric  $H_2/O_2$  gas mixture, and (ii) to find out whether or not the addition of catalysts for the oxygen reaction, such as active carbon and carbon activated with pyrolyzed metal chelates or silver, to the electrodes for recombination of  $H_2/O_2$  gas mixture affects the corrosion resistance of WC.

## Experimental

### *Methods for electrode preparation and for measuring their activity*

The experiments were carried out with carbides synthesized from  $WO_3$  ( $S_{BET} = 17 \text{ m}^2 \text{ g}^{-1}$ ) in carbon monoxide atmosphere at different temperatures according to a previously described method [6]. WC with various specific surfaces ( $S_{BET}$ ), respectively, various grain sizes, were selected for the investigations. The other factors that might influence the rate of WC corrosion, e.g., the carbon content in the crystal lattice ( $C_{bonded}$ ) and the free carbon deposited over the carbide particles ( $C_{free}$ ) had constant values:  $C_{bonded} = 5.10\text{--}5.20 \text{ wt.}\%$  and  $C_{free} = 0.11\text{--}0.12 \text{ wt.}\%$ , respectively. Determination of the quantities of  $C_{bonded}$  and  $C_{free}$  was performed by the method presented in ref. 6. Series of electrodes with an apparent surface of  $1 \text{ cm}^2$  were prepared from the carbides under investigation. For catalyzing the oxygen reaction, besides pure WC, other catalysts such as Ag formed on the surface of WC [7], Norit NK active carbon and  $KM_2$  active carbon catalyzed additionally with 20 wt.% of pyrolyzed tetraazaanulene (TAA), were also added. The catalyst mixtures used are presented in Table 1.

The mixture of catalyst/binder (powder polytetrafluoroethylene (PTFE)) was pressed at  $320 \text{ }^\circ\text{C}$  over lead grids with an area of  $1 \text{ cm}^2$ . The electrodes from each series (8 electrodes in a series) were placed in separate electrochemical cells, partially immersed in  $H_2SO_4$ , sp. gr. 1.28. The cell lids were fitted with tubes for blowing a stoichiometric hydrogen/oxygen gas mixture obtained from alkaline electrolyzers. The electrode potentials were measured versus  $Hg/Hg_2SO_4$  reference electrode and then recalculated versus HE. Every 1000 h the cells were opened and one electrode from the respective series was taken out. Adjustment of the electrolyte level and density was performed before sealing the cell again. The catalytic activity of the electrodes taken out was measured and the chemical composition of the carbides was determined.

The electrode activity was evaluated by measuring the rate of recombination of hydrogen and oxygen on each electrode. This rate was calculated as the difference between the quantities of gas mixture going into and out of the cell per hour divided by the geometrical surface of the electrode.

TABLE 1

Catalyst mixtures used for the preparation of test of tungsten carbide electrodes

No.	Tungsten carbide		Silver (wt.%)	Norit NK (mg)	KM <sub>2</sub> +TAA (mg)
	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	quantity (mg)			
1	3.0	100			
2	7.0	100			
3	7.0	100		5	
4	7.0	100			5
5	10.5	100	2		
6	10.5	100	2	5	
7	10.5	100	2		5
8	13.0	100			

The phase composition of the electrodes was established through X-ray analysis, and the WO<sub>x</sub> content was determined by weight measurements [4]. The electrode material (catalyst + binder) was scraped off the lead grid and treated with 20% KOH solution at 60 °C for 15 min. Oxides dissolved during this treatment [8]. After washing until neutral reaction and drying, the weight losses were used for evaluating the quantity of oxides, expressed in wt.% of the total catalyst quantity. The accuracy of this method is ± 1–2%.

## Results and discussion

### *Corrosion resistance of tungsten carbide recombination electrodes with different active surfaces*

To study the influence of the WC specific surface on its corrosion rate, the changes in recombination rate and the quantities of WO<sub>x</sub> formed were measured for electrodes with specific surfaces of 3, 7 and 13 m<sup>2</sup> g<sup>-1</sup> (samples nos. 1, 2 and 8). The results obtained are presented in Fig. 1.

As seen from this Fig. no proportional dependence exists between the electrode activity with respect to the recombination of stoichiometric H<sub>2</sub>/O<sub>2</sub> gas mixture and their specific surface. A similar effect was also observed when measuring the WC activity with respect to the hydrogen reaction for WC contents above 40 mg cm<sup>-2</sup> [9]. This could be explained by screening of part of the catalyst particles. To verify this assumption, the charging curves of electrodes catalyzed with WC (S<sub>BET</sub>=7 and 13 m<sup>2</sup> g<sup>-1</sup>, nos. 2 and 8) were recorded within the potential interval between +150 and +350 mV after the method described in ref. 6. The capacity of the double layer was assumed to be 150 μF cm<sup>-2</sup> of electrode apparent surface [10]. The calculated electrode surfaces were 3000 cm<sup>2</sup> for electrode no. 2 and 3300 cm<sup>2</sup> for electrode no. 8, respectively. These close values of the active surfaces can explain the almost equal catalytic activity of the electrodes. After about 2000 h, the activity of electrodes catalyzed with WC, S<sub>BET</sub>=7 and 13 m<sup>2</sup> g<sup>-1</sup>, declines significantly (from 12–15 cm<sup>3</sup> h<sup>-1</sup> cm<sup>-2</sup> to about 4 cm<sup>3</sup> h<sup>-1</sup> cm<sup>-2</sup>), while the activity of electrodes prepared from WC with small specific surface is reduced from 8 cm<sup>3</sup> h<sup>-1</sup> cm<sup>-2</sup> to 5 cm<sup>3</sup> h<sup>-1</sup> cm<sup>-2</sup>. After another 2000 h, the recombination rate of the first two series of electrodes

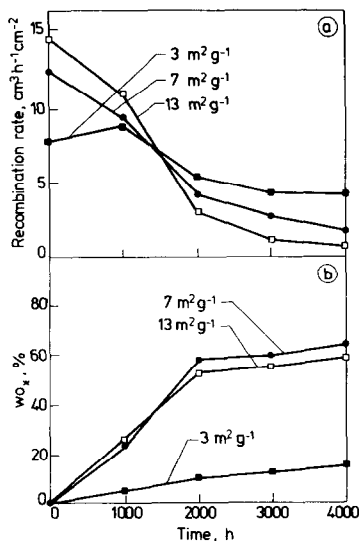


Fig. 1. (a) Recombination rate and (b)  $\text{WO}_x$  content of tungsten carbide electrodes as a function of the time of blowing through with  $\text{H}_2/\text{O}_2$  gas mixture.

decreases further (below  $2 \text{ cm}^3 \text{h}^{-1} \text{cm}^{-2}$ ), while that of the small surface WC catalyzed electrodes remains almost unchanged. As seen from Fig. 1(b), the WC activity is directly related to the  $\text{WO}_x$  content, i.e., to the corrosion resistance of the catalyst. WC with large specific surface corrodes at a considerably higher rate (the  $\text{WO}_x$  content after 2000 h reaches 60%) and its recombination rate decreases more than five times, while the oxidation of WC with small specific surface for the same time interval is very low, about 10%. After 4000 h, the oxide content in these electrodes is below 15% and hence they preserve their catalytic activity. Figure 1(b) shows also that WC with  $S_{\text{BET}} = 7$  and  $13 \text{ m}^2 \text{g}^{-1}$  corrode at the same rate under the experimental conditions applied. This finding apparently contradicts the above statement that the corrosion resistance of the carbides selected for the investigation is a function of their specific surface. As noted above, after the sintering procedure, the two electrodes participate in the corrosion process with almost equal active surfaces, which determines the similar rates of their corrosion.

#### *Corrosion resistance of tungsten carbide in the presence of active carbon*

As established in our previous studies, the addition of active carbon to WC in the catalytic electrodes for recombination of  $\text{H}_2/\text{O}_2$  gas mixtures improves the initial electrode activity with respect to the oxygen reaction [2]. This, together with the better gas supply in the presence of small quantities of active carbon [11], causes the recombination rate to increase. On the other hand, adding active carbon to WC can occasionally lead to a decrease in activity of this catalytic mixture with respect to the hydrogen reaction due to the relative decrease in WC content in the catalytic mixture and to the changed structure of the catalytic layer. To determine the optimum ratio between WC and active carbon in the catalytic mixture, the recombination rates were measured for electrodes containing  $100 \text{ mg cm}^{-2}$  WC and various amounts of Norit NK (0–12  $\text{mg cm}^{-2}$ ). The results obtained for the activity of WC with  $S_{\text{BET}} = 7 \text{ m}^2 \text{g}^{-1}$  are presented in Fig. 2.

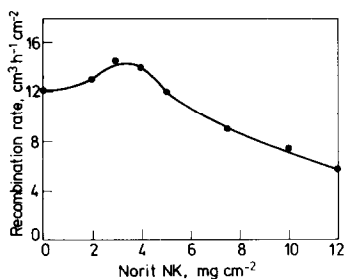


Fig. 2. Recombination rate as a function of the content of Norit NK active carbon.

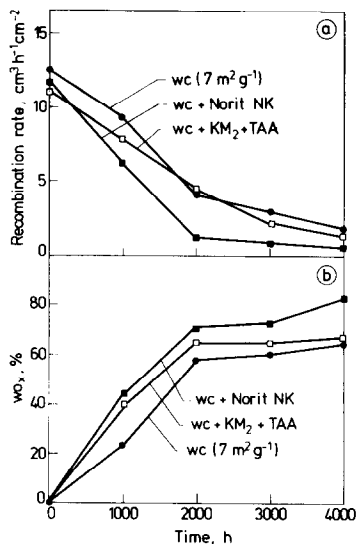


Fig. 3. (a) Dependence of the recombination rate and (b) the  $WO_x$  content of tungsten carbide electrodes containing active carbon on the time of testing.

This Fig. shows that the optimum content of Norit NK carbon yielding the highest electrode activity is about  $3 \text{ mg cm}^{-2}$ . Electrodes containing  $5 \text{ mg cm}^{-2}$  WC exhibit an activity almost the same as that of electrodes without active carbon.

To investigate the corrosion resistance of the catalytic mixture WC + active carbon, electrodes were prepared containing WC with an active surface of  $7 \text{ m}^2 \text{ g}^{-1}$  and Norit NK active carbon, and WC and  $KM_2$  active carbon with 20% TAA (samples nos. 2, 3 and 4). Such a WC/active carbon ratio was selected that gave almost equal initial recombination rates for the three series of electrodes. The results obtained from measuring the recombination rate and the  $WO_x$  contents are presented in Fig. 3.

This Fig. shows that the presence of Norit NK active carbon causes the catalyst corrosion rate to grow as a result of which the activity of the catalyst mixture WC + Norit NK decreases more quickly than that of the activity of pure WC catalysts. The catalyst mixture  $KM_2$  active carbon + 20% TAA exerts a weaker influence on the activity of the catalyst.

#### *Corrosion resistance of tungsten carbide catalysts containing silver*

Silver is one the most efficient catalysts at the second stage of the oxygen reaction, i.e., the decomposition of hydrogen peroxide [12]. To study the effect of Ag on WC corrosion, electrodes were prepared containing WC (with a specific surface of  $10.5 \text{ m}^2 \text{ g}^{-1}$ ) and 2 wt.% Ag (sample no. 5). The influence of active carbon on the corrosion of WC in the presence of Ag was also investigated (samples nos. 6 and 7). The results obtained are presented in Fig. 4.

Silver increases significantly the corrosion resistance of WC. After 2000 h, the  $WO_x$  content is about 20%, and after 4000 h it amounts to about 30%, while nonsilver-containing electrodes catalyzed with WC,  $S_{BET} = 7 \text{ m}^2 \text{ g}^{-1}$  (Fig. 1), contain about 60% of  $WO_x$ . The highest rate of recombination for the whole investigation period was

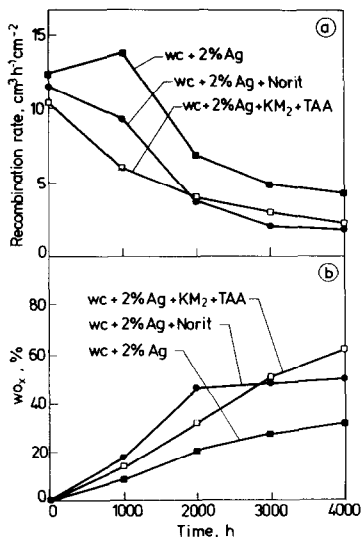


Fig. 4. (a) Dependence of the recombination rate and (b) the  $WO_x$  content of tungsten carbide electrodes with additions of silver and active carbon on the time of testing.

measured with electrodes containing only WC and Ag. The addition of active carbon (Norit NK or  $KM_2 + 20\%$  TAA) neutralizes the positive effect of Ag, and electrodes containing Ag + active carbon corrode quickly, which leads consequently to low catalytic activity.

#### Summary of the results

The results of previous investigations in our laboratory [2] suggest that during  $H_2$  and  $O_2$  recombination, microgalvanic elements of short-circuited hydrogen and oxygen electrodes are formed on the surface. At these surface sites, the reactions typical for hydrogen and oxygen electrodes in acidic solution proceed:



Hydrogen peroxide is known to be stable in acidic medium and it is obviously possible for the  $H_2O_2$  obtained as an intermediate product (eqn. 2) to accumulate in the electrolyte. The above mentioned investigation [2] showed also that WC introduced into the electrolyte catalyzes the decomposition of  $H_2O_2$ . Oxidation of WC was also observed proceeding probably through the following reaction:



Based on these considerations the results of the present investigation can be analysed and compared with the data obtained earlier [4].

Table 2 presents some of the data on the corrosion resistance of WC flooded with battery  $H_2SO_4$  (nos. 1 and 2) reported in ref. 4 and some of the results (nos. 3, 4 and 5) from the present investigation on WC corrosion for the case of recombination of hydrogen and oxygen on WC electrodes partially immersed in battery  $H_2SO_4$ .

TABLE 2

Corrosion test results for tungsten carbide electrodes with different specific surfaces

Conditions	No.	Composition	WC $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	WO <sub>x</sub> (%)		$\varphi_{\text{WC}}^{\text{a}}$ (mV) (HE)
				1000 h	2000 h	
Immersed in H <sub>2</sub> SO <sub>4</sub>	1 <sup>b</sup>	WC	4.26	5.5	10.0	432
air atmosphere	2 <sup>b</sup>	WC	10.38	11.0	21.0	500
Partially immersed	3	WC	3.0	6.0	11.0	382
in H <sub>2</sub> SO <sub>4</sub>	4	WC	7.0	23.2	58.2	370
H <sub>2</sub> /O <sub>2</sub> gas mixture	5	WC + Ag	10.5	10.0	20.4	357

<sup>a</sup>Electrode potentials were measured at the 24th h of testing.<sup>b</sup>Results reported in ref. 4.

As seen from Table 2, when recombination of hydrogen and oxygen occurs (nos. 3 and 4), in spite of the fact that the catalyst specific surface is smaller, the rate of WC corrosion is higher than in the case of WC oxidation under the action of oxygen dissolved in the acid (nos. 1 and 2). However, knowing that the concentration of oxygen in the gas mixture is several times higher than that of the oxygen dissolved in the electrolyte, it can be concluded that the corrosion rate of WC under the present experimental conditions is much lower (especially so for WC with low specific surfaces). The difference in the rate of corrosion under the different conditions is probably due to the different corrosion potentials measured on the WC surface in the presence of H<sub>2</sub> (nos. 3 and 4) or when no H<sub>2</sub> is present (nos. 1 and 2).

On comparing the corrosion resistance of WC with various surfaces on recombination of the H<sub>2</sub>/O<sub>2</sub> gas mixture (nos. 3 and 4) it can be seen that the samples with twice the surface (no. 4) have 4 to 5 times lower corrosion resistance. The initial rates of recombination for the two types of carbides differ by about 60 to 70%, but after 1000 h they become practically equal. Hence, the different corrosion rates could be assigned to different particle sizes, different degrees of segregation between them and different number of crystal defects. These are the reasons why after 2000 h of recombination of the gas mixture, the WO<sub>x</sub> content in electrodes catalyzed with larger specific surface WC (no. 4) reaches 60 to 70%. During the next 2000 h, almost no further increase in the content of oxides in these electrodes is observed. This considerable decline in the rate of WC corrosion may have two possible explanations. On the one hand, the recombination rate decreases abruptly (from 12 to 15 cm<sup>3</sup> h<sup>-1</sup> cm<sup>-2</sup> at the beginning down to 2 to 3 cm<sup>3</sup> h<sup>-1</sup> cm<sup>-2</sup> after 2000 h of testing), which leads to a significant decrease in the amount of H<sub>2</sub>O<sub>2</sub> formed as a result of the recombination. On the other hand, the great quantity of WO<sub>x</sub> may form a passivating or screening layer on the surface of WC particles, which would impede further their oxidation.

It has been established that active carbon as well as the mixture active carbon + pyrolyzed TAA products have a stronger catalytic effect on the first stage of oxygen reduction, i.e., the formation of H<sub>2</sub>O<sub>2</sub> (eqn. (2)) [13]. The presence of carbon probably affects the equilibrium between the formation and decomposition of H<sub>2</sub>O<sub>2</sub> in favour of the first reaction, which results in the decomposition of part of the H<sub>2</sub>O<sub>2</sub> generated on the active carbon surface and hence the corrosion rate grows.

Silver is an active catalyst of H<sub>2</sub>O<sub>2</sub> decomposition [12]. When Ag is added to WC it causes an increase in activity of the recombination electrodes, on the one hand, and a considerable decrease in WC corrosion, on the other hand (Fig. 4). The data

in Table 2 (nos. 2 and 5) show that a 2% addition of Ag to the WC catalyst does not change the corrosion rate of these electrodes under the action of the gas mixture as compared to that of pure WC in  $H_2SO_4$ . These results can be explained with the significantly higher rate of decomposition of  $H_2O_2$  in the presence of Ag.

The situation changes when active carbon is added to the catalyst mixture WC+ Ag, in this case in an amount exceeding by far that of Ag. Active carbon exerts such a strong effect that it almost neutralizes the anticorrosion effect of Ag, and hence intense oxidation of WC is observed in the presence of both active carbon and Ag, which is almost equal to the oxidation of pure WC.

## Conclusions

The results obtained show that on prolonged recombination of stoichiometric  $H_2/O_2$  gas mixture on the WC electrodes, certain corrosion processes occur as a result of which the  $WO_x$  content may reach 60 to 70% after 2000 h of electrode operation. It has been established that the oxidation of WC is caused by the  $H_2O_2$  formed as an intermediate product of the recombination of hydrogen and oxygen. The use of catalysts (for example Ag) facilitating the decomposition of  $H_2O_2$ , reduces significantly the corrosion of WC, whereas catalysts (like active carbon) that activate more notably the first stage of the oxygen reaction, enhance the oxidation of WC on recombination of the  $H_2/O_2$  gas mixture.

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