

## TUNGSTEN CARBIDE ELECTRODES FOR GAS RECOMBINATION IN LEAD/ACID BATTERIES

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### Introduction

The main reactions associated with current generation in the lead/acid battery are accompanied by electrochemical decomposition of water. As a result, the battery must be regularly topped up with water, *i.e.*, the lead/acid battery requires maintenance.

In principle, two methods have been developed to reduce water loss during battery operation. The first involves increasing the overvoltage of hydrogen and oxygen evolution, and limiting the charge voltage to below the voltage of water decomposition. The second approach to maintenance-free operation is to encourage the recombination of the hydrogen and oxygen released in the cell. This can be achieved through: (i) an oxygen cycle, whereby the positive plate is charged first, and before the beginning of the hydrogen evolution, so that the oxygen released on the positive plate is reduced on the negative; (ii) the use of catalytic plugs containing noble metals (*e.g.*, platinum, palladium, ruthenium) to recombine the gases to water. In the latter case, the plug is mounted on the lid of each cell [1 - 4]. Since the reaction of hydrogen and oxygen with the plug catalyst is purely a chemical reaction, the gases combine in stoichiometric amounts. During battery operation, however, hydrogen and oxygen can be released in a non-stoichiometric ratio. To prevent pressure increase in such a situation, the gases have to be vented to the atmosphere; this leads to water loss.

The above disadvantage has been overcome by using partially-immersed catalytic electrodes. Noble metals are used as the catalysts. These electrodes are connected with the lead and/or the lead dioxide electrode of the cell in such a way as to ensure a suitable potential region for the reactions of oxygen reduction and hydrogen oxidation to proceed [5]. When employing these auxiliary electrodes in the cells, however, a partial dissolution of the noble metals in the electrolyte often occurs. The noble metal ions deposit on the surface of the lead and lead dioxide plates, and thus cause an increase in the self-discharge and sulphation of the plates. The high cost of noble metals

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is a further disadvantage. For these reasons, such devices have not found application in the battery industry.

In the 1970s, it was established that tungsten carbide (WC) had good catalytic activity towards hydrogen oxidation in sulphuric acid solution [6, 7]. Though the catalytic activity of WC is lower than that of platinum, by enlarging the surface of the electrodes (*i.e.*, the amount of WC) the activity becomes adequate for the oxidation of hydrogen. Tungsten carbide has been used, therefore, as a catalyst in hydrogen gas-diffusion electrodes for fuel cells [8]. The advantage of WC over platinum is that the material is less sensitive to impurities in the cell [6].

An attempt was made to mount WC electrodes in lead/acid cells for oxidation of the released hydrogen [9]. The corrosion products of WC electrodes have little influence on the rate of hydrogen evolution. Hence, their deposition on the lead or lead dioxide plate does not intensify the self-discharge rate; this is a very important advantage. There still remains, however, the problem of oxygen evolution. In practice, it is not possible to prevent the release of oxygen since evolution of the gas commences when the positive plate reaches 65 - 70% state-of-charge [10]. The coefficient of utilization of the positive active material of such a battery will be very low. Therefore, the catalytic electrodes used in sealed batteries should also be active towards oxygen reduction. There are no published data available on the catalytic activity of WC towards oxygen reduction.

The aims of the present study are:

- (i) to establish whether WC electrodes in sulphuric acid solution are catalytically active towards oxygen reduction;
- (ii) following success in (i) above, to establish the feasibility of such electrodes for the recombination of hydrogen and oxygen released during the operation of lead/acid batteries.

## Experimental

The technology and design of the WC catalytic electrodes have been published previously [11 - 13]. The partially-immersed electrodes consisted of an electro-conductive lead grid on to which the catalytically active material was pressed. The active material contained catalyst and binder. The catalyst was tungsten carbide powder (WC) or a mixture of WC and active carbon. The latter exhibits catalytic activity towards the reduction of oxygen. Teflonized carbon black was used as binder.

Studies were carried out using the experimental cell shown in Fig. 1. The potential of the WC electrode was measured *versus* an Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode. A lead plate was used as a counter electrode. The electrolyte was H<sub>2</sub>SO<sub>4</sub> of sp. gr. 1.28. One-fifth of the electrode surface was immersed in the electrolyte. The recombination rate of hydrogen and oxygen on the WC electrode was evaluated from the difference between the amounts of the incoming and outgoing gas mixtures, as determined by flowmeters.

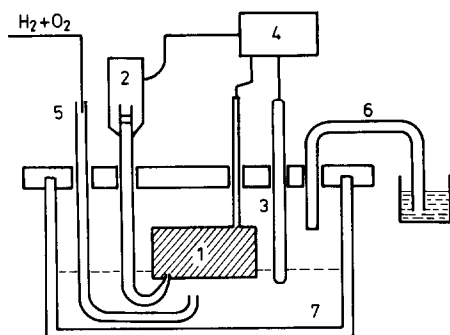


Fig. 1. Experimental cell for measuring performance of partially-immersed electrodes: 1, WC; 2, Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode; 3, lead counter electrode; 4, potentiostat; 5, gas inlet; 6, gas outlet; 7, electrolyte, H<sub>2</sub>SO<sub>4</sub> sp. gr., 1.28.

Long-term tests of the WC catalytic electrodes were performed in a 12 V/84 A h traction battery. Five of the cells contained three WC electrodes, each mounted on the cell cover. The total surface area of these electrodes was 90 cm<sup>2</sup>. The sixth cell did not contain auxiliary electrodes and was used to assess the gas amounts released during the test.

Measurements were carried out to determine:

- (i) the volt-ampere dependences of the oxygen and hydrogen reactions proceeding on the partially-immersed electrodes; for this purpose, oxygen and hydrogen were fed in succession into the cell, the potential of the WC electrode was maintained with a potentiostat, and the current density was measured under steady-state conditions;
- (ii) the potential of the WC electrode on open circuit as a function of the hydrogen/oxygen ratio in the gas mixture;
- (iii) the recombination rate of hydrogen and oxygen on open circuit as a function of temperature or concentration of sulphuric acid;
- (iv) the life span of the catalytic auxiliary electrodes at continuous overcharge in a 12 V/84 A h battery.

## Results

### *Volt-ampere characteristics of partially-immersed electrodes*

A study was made of electrodes catalyzed with either WC (200 mg cm<sup>-2</sup>) alone or with a WC (200 mg cm<sup>-2</sup>) and active carbon (10 mg cm<sup>-2</sup>) mixture. The volt-ampere curve of electrodes catalyzed with 6 mg cm<sup>-2</sup> of platinum was taken for comparison purposes. The volt-ampere curves of the three types of electrodes are presented in Fig. 2. The following conclusions can be drawn from the data.

- (i) The catalytic activity of WC towards oxygen reduction is commensurate with its activity towards hydrogen oxidation. This discovery suggests that WC is a suitable material for the development of electrodes for the

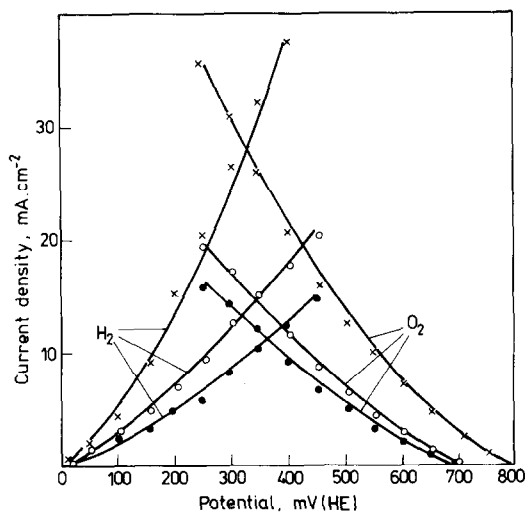


Fig. 2. Volt-ampere characteristics of  $H_2$  and  $O_2$  reactions on partially-immersed electrodes containing different catalysts: ●, WC ( $200 \text{ mg cm}^{-2}$ ); ○, WC + C ( $200 \text{ mg cm}^{-2} + 10 \text{ mg cm}^{-2}$ ); ×, C + Pt ( $100 \text{ mg cm}^{-2} + 6 \text{ mg cm}^{-2}$ ). Temperature,  $30^\circ\text{C}$ ;  $H_2SO_4$  sp. gr., 1.28.

recombination of gas mixtures released during the operation of lead/acid batteries.

(ii) When active carbon is added to the tungsten carbide, the catalytic activity increases towards both the oxygen and the hydrogen reactions. A similar effect has been observed [14] for the activity of gas-diffusion electrodes catalyzed with tungsten carbide with regard to the hydrogen reaction. The increased activity of the electrodes is due to an improved gas transport in the reaction layer [14]. All further studies in the work reported here were performed with electrodes containing a mixture of tungsten carbide and active carbon (WC + C) as catalyst.

(iii) The activity of the electrode catalyzed with platinum is twice that of the (WC + C) electrode. By doubling the surface area of the (WC + C) electrode, it is possible for its catalytic activity to rival that of a platinum electrode. The lower price of tungsten carbide allows the application of such auxiliary electrodes in lead/acid batteries.

(iv) At the intersection of the volt-ampere curves, the reaction rates of oxygen reduction and hydrogen oxidation are equal (Fig. 2). The potential corresponding to this point is shifted towards more negative values for electrodes in the following order: WC > (WC + C) > Pt.

This behaviour shows that the rate of hydrogen oxidation increases faster than that of oxygen reduction.

#### *Dependence of electrode potential and recombination rate on $H_2/O_2$ ratio*

The steady-state electrode potential on open circuit depends on the ratio between the partial pressures of hydrogen and oxygen. Figure 3 pre-

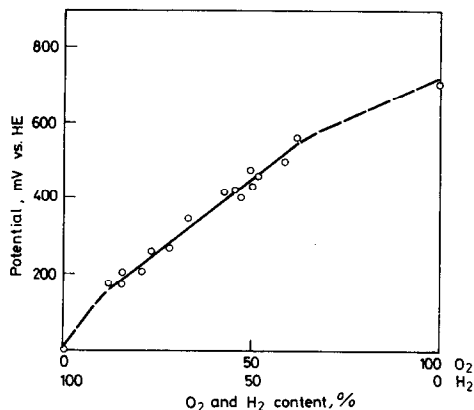


Fig. 3. Dependence of steady-state potential of partially-immersed electrode on  $H_2/O_2$  ratio in gas mixture. Catalyst =  $200 \text{ mg cm}^{-2} \text{ WC} + 10 \text{ mg cm}^{-2} \text{ C}$ ; temperature,  $30^\circ \text{C}$ ;  $H_2SO_4$  sp. gr., 1.28.

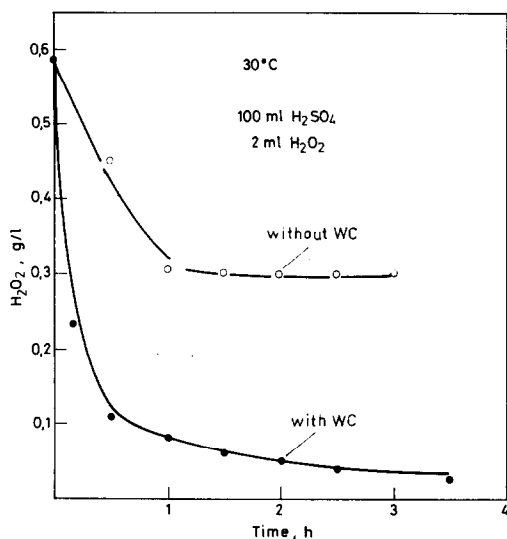


Fig. 4. Change in  $H_2O_2$  concentration in  $H_2SO_4$  solution with, and without, WC catalyst.

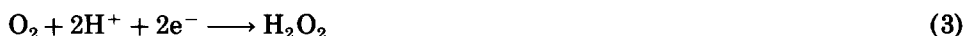
sents the dependence of the potential of the (WC + C) electrode on the amounts of hydrogen and oxygen in the gas mixture. The investigations were carried out in gas mixtures containing 10 - 60% oxygen. It can be seen that the potential increases approximately linearly with increase in the amount of oxygen in the gas mixture. The oxygen equilibrium potential on platinum for the reaction:



is given by:

$$\phi = 1.23 + 0.023 \log(P_{O_2} [a_{H^+}]^4 / [a_{H_2O}]^2) \quad (2)$$

The value of the normal potential is +1230 mV *versus* a hydrogen electrode (HE). Figure 3 shows, however, a value of +700 mV. This is approximately the value of the equilibrium potential of an electrode on which oxygen is reduced to hydrogen peroxide, *i.e.*,



$$\phi = 0.682 + 0.059 \log(P_{O_2} [a_{H^+}]^2 / a_{H_2O_2}) \quad (4)$$

It follows that hydrogen peroxide will accumulate in the electrolyte during oxygen reduction on the WC electrode. This will be true only if WC does not catalyze the decomposition of  $H_2O_2$ .

The kinetics of  $H_2O_2$  decomposition in the presence of WC was investigated. A 1 g sample of WC was added to 100 ml of  $H_2SO_4$  (sp. gr. 1.28) containing 6 g of  $H_2O_2$ . The change in  $H_2O_2$  concentration with, and without, WC was followed, see Fig. 4. It can be seen that WC is an effective catalyst for the decomposition of  $H_2O_2$ . Therefore, the  $H_2O_2$  formed during oxygen reduction will not accumulate in the electrolyte, thus preventing self-discharge of the negative plate.

Since both the hydrogen and the oxygen reactions occur on the (WC + C) electrode, a recombination reaction will take place when this electrode is in contact with a mixture of the two gases, *i.e.*,



The dependence of the rate of reaction (5) on the ratio of hydrogen to oxygen was investigated. The results are shown in Fig. 5. The data indicate that the recombination reaction reaches a maximum rate at a stoichiometric ratio of 2:1 between hydrogen and oxygen. Any deviation from this gas ratio in either direction decreases the recombination rate. The potential of the (WC + C) electrode at the maximum recombination rate is +320 mV (HE).

#### *Determination of activation energy for $H_2/O_2$ recombination on WC electrodes*

The study was performed at the maximum reaction rate (*i.e.*,  $H_2:O_2 = 2:1$ ). The electrolyte temperature was varied between 10 and 50 °C. Figure 6 presents the temperature dependence of the recombination rate in Arrhenius coordinates. A good linear relationship is observed; the correlation coefficient is 0.985. The estimated activation energy from the slope of the straight line is equal to 3.7 kcal mol<sup>-1</sup>. This value is low and suggests that the rate-determining stage of the recombination reaction is slow transport of the reacting gases and/or the reaction products.

#### *Dependence of recombination rate on $H_2SO_4$ concentration*

During operation of the lead/acid battery, the electrolyte concentration changes from 5.2 to 0.8 mol l<sup>-1</sup>. It is important, therefore, to establish the dependence of the catalytic activity of a (WC + C) electrode on this parameter.

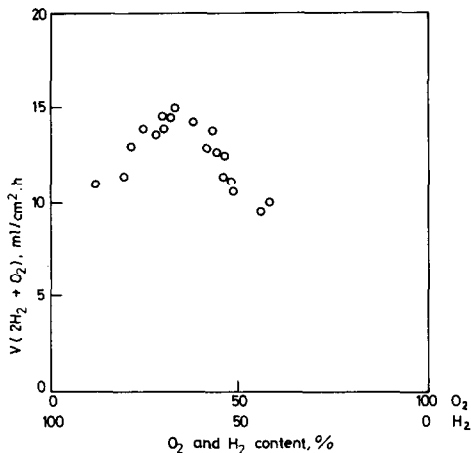


Fig. 5. Dependence of recombination rate on H<sub>2</sub>/O<sub>2</sub> ratio.

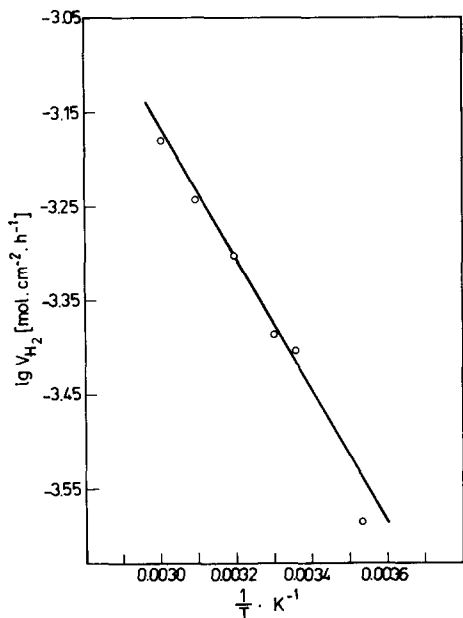


Fig. 6. Temperature dependence of recombination rate in Arrhenius coordinates. Catalyst = 200 mg cm<sup>-2</sup> WC + 10 mg cm<sup>-2</sup> C; H<sub>2</sub>SO<sub>4</sub> sp.gr. 1.28.

A 2:1 gas mixture of H<sub>2</sub> and O<sub>2</sub> was used for this study. The (WC + C) electrode was left at open circuit. The data given in Fig. 7 demonstrate that the gas recombination rate decreases linearly with increase in H<sub>2</sub>SO<sub>4</sub> concentration. This dependence can be related to transport hindrances: the solubility of both hydrogen and oxygen decreases with increase in H<sub>2</sub>SO<sub>4</sub> concentration.

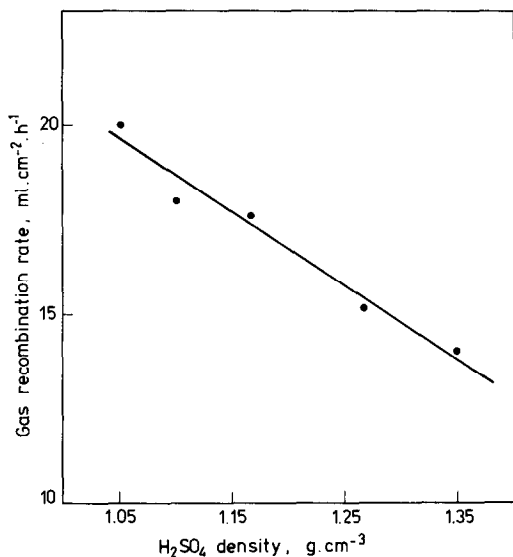


Fig. 7. Dependence of recombination rate on H<sub>2</sub>SO<sub>4</sub> acid concentration. Catalyst = 200 mg cm<sup>-2</sup> WC + 10 mg cm<sup>-2</sup> C; temperature, 25 °C.

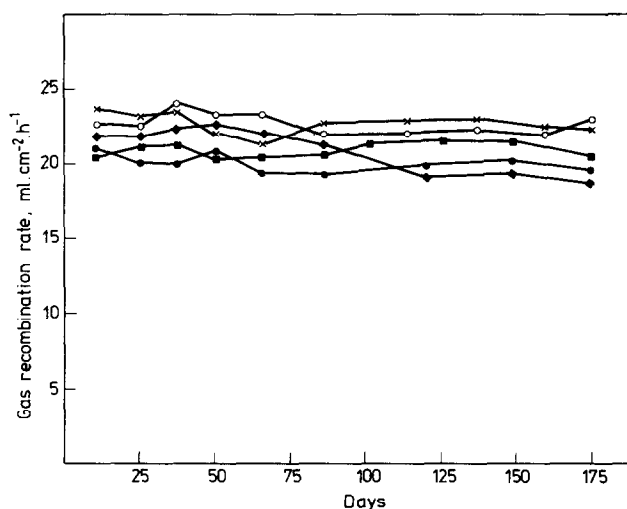


Fig. 8. Recombination rate during long-term tests of auxiliary electrodes in 12 V/84 A h battery. Catalyst, 200 mg cm<sup>-2</sup> WC + 10 mg cm<sup>-2</sup> C; temperature, 30 °C; cells 1: x; 2: O; 3: ●; 4: ■; 5: ◆.

Charged stationary and traction batteries usually operate in H<sub>2</sub>SO<sub>4</sub> solutions of sp. gr. 1.22 and 1.28, respectively. According to Fig. 7, the catalytic activity of a (WC + C) electrode in stationary batteries is about 15% higher than that in traction batteries.



### *Durability of recombination (WC + C) electrodes in batteries*

A set of three (WC + C) electrodes was mounted in each of the five cells of an 84 A h lead/acid battery. The battery was maintained under float overcharge conditions with a current of 3 A. This value was chosen so that 10% of the released gases were not recombined, *i.e.*, the catalytic electrodes operated with maximum efficiency. The recombination rate was determined by measuring the volume of unreacted gases at regular intervals. The test was carried out for 170 days. The results are summarized in Fig. 8.

It can be seen that the activity of the (WC + C) electrode remained roughly unchanged during these 170 days. After this period, the catalytic electrodes were subjected to X-ray diffraction and wet chemical analyses. It was established that 5 - 7% of the tungsten carbide was oxidized during the 170 days of operation.

### Conclusions

The above results show that catalytic (WC + C) electrodes will allow maintenance-free operation of stationary lead/acid batteries under float overcharge service. The required surface area of the catalytic electrodes is determined by the overcharge current of the battery. Each unit area ( $\text{cm}^2$ ) of the auxiliary electrode can recombine fully the gases released in the lead/acid cell at a current of about 25 mA. To all intents and purposes, this value meets the requirements of lead/acid battery overcharge and thus prevents loss of water.

### References

- 1 S. Akira, Y. Makoto and M. Masao, *Jap. Pat. No. 44-41 239* (May 23, 1969).
- 2 T. Akio and M. Sindzi, *Jap. Pat. No. 48-27 540* (Feb. 14, 1972).
- 3 S. Akira, Y. Makoto and M. Masao, *Jap. Pat. No. 43-68 980* (Sept. 19, 1968).
- 4 T. Akio and T. Masamiti, *Jap. Pat. No. 48-121 398* (Oct. 29, 1973).
- 5 P. Reutschi and J. Ockerman, *Electrochem. Technol.*, 4 (1966) 383.
- 6 H. Bohm and F. Pohl, *Troisieme Journee Internat. d'Etude des piles a Combustible, Bruxelles, 1969*, p. 183.
- 7 H. Bohm, *Electrochim. Acta*, 15 (1970) 1273.
- 8 R. Fleischman and H. Bohm, *Ber. Bunsenges. Phys. Chem.*, 84 (1980) 1023.
- 9 M. Jung, *Ger. Pat. No. 2,312,131* (Mar. 12, 1973).
- 10 K. Peters, A. I. Harrison and W. H. Durant, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1968, p. 1.
- 11 I. Nikolov, V. Nikolova and T. Vitanov, *J. Power Sources*, 4 (1979) 65.
- 12 I. Nikolov, V. Nikolova and T. Vitanov, *J. Power Sources*, 7 (1981/82) 83.
- 13 *Br. Pat. No. 73,149*.
- 14 I. Nikolov, M. Svata, L. Grigorov, T. Vitanov and Z. Zabransky, *J. Power Sources*, 3 (1978) 237.