Performance of tungsten carbide recombination electrodes under various operating conditions

I. Nikolov, G. Papazov* and V. Najdenov

*Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 1040 (Bulgaria)*

Abstract

The performance of tungsten carbide (WC) recombination electrodes in lead/acid batteries with flooded, gelled or immobilized electrolytes has been investigated under various operating conditions. It has been established that the rate of recombination of hydrogen and oxygen on WC electrodes mounted in batteries with immobilized and gelled electrolytes is considerably higher than that on partially immersed electrodes in flooded batteries. This increase in the recombination rate is due to the increased temperature of the WC electrodes as a result of the exothermal process of water formation. When partially immersed electrodes are used, a heat exchange takes place between the electrodes and the electrolyte and hence the rate of recombination grows. If, however, the recombination electrodes are not in contact with the electrolyte and the recombination rate reaches values higher than $200 \ cm^3 \ h^{-1} \ cm^{-2}$, the hydrogen/oxygen gas mixture may explode.

Introduction

On charging of lead/acid battery positive and negative plates, parallel electrochemical reactions of oxygen and hydrogen evolution proceed. This intense gassing poses serious problems when sealing of the battery is attempted. One of the possible approaches to the manufacture of maintenance-free batteries is to employ catalytic plugs containing noble metals (e.g., platinum, palladium, ruthenium) on which recombination of hydrogen and oxygen takes place. To prevent catalyst particles from dissolving in the electrolyte, which would reduce significantly the overvoltage of hydrogen and oxygen evolution and hence cause intense gassing, the plugs are mounted on the lid of each cell. The reaction of hydrogen and oxygen is accompanied by considerable heat release:

$$H_2(g) + 1/2O_2(g) \rightleftharpoons H_2O(l) + 242.4 \ kJ \ mol^{-1} \tag{1}$$
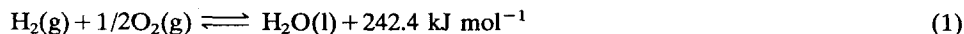
It can be calculated that each A h of cell overcharge yields 4.52 kJ as a result of gas recombination. This causes overheating of the catalytic plug, which may lead to an explosion of the H_2/O_2 gas mixture and consequent battery failure. To avoid this hazard, the battery cell design should ensure adequate heat exchange between the built-in recombination electrode and the surrounding medium.

Our investigations have shown [1, 2] that partially-immersed electrodes containing tungsten carbide (WC) as catalyst can be used for recombination of hydrogen and

---

*Author to whom correspondence should be addressed.

oxygen. This catalytic material has a sufficiently high activity to find practical application in lead/acid batteries. Its main advantage over noble metals used as catalysts is that its particles, when dissolved in the electrolyte or deposited on the battery plates, do not cause intense gassing [1].

The aim of the present investigation was to study the performance of WC recombination electrodes set in lead/acid batteries with gelled or glass-mat immobilized electrolytes.

Experimental

Recombination electrodes with an apparent surface of 30 cm^2 were used. The electrodes consisted of an electroconductive lead grid onto which the catalyst and binder were pressed. The catalyst used was WC with BET surface $S_{BET} = 2.7$ m^2 g^{-1} in an amount of 500 mg cm^{-2}. These electrodes were partially immersed in H$_2$SO$_4$ (sp.gr. 1.28) and their potential/current characteristics in gas mixtures H$_2$/Ar and O$_2$/Ar were determined galvanostatically. Potential measurements were carried out versus a Hg/Hg$_2$SO$_4$ reference electrode and then the measured values recalculated versus HE. Sample recombination electrodes from this series were sent for testing at Johnson Controls, Inc., Milwaukee, WI, USA [3].

The investigations were carried out using an experimental cell fed with a stoichiometric H$_2$/O$_2$ gas mixture from an electrolyser at a constant flow rate of 3700 cm^3 h^{-1}. This gas flow corresponds to the gases released at an overcharge current of 5 A. The following experimental setups were used:

(i) the experimental cell contained one WC electrode partially (20%) immersed in H$_2$SO$_4$ solution, sp.gr. 1.28;

(ii) two positive and three negative plates separated by glass-mat separators were placed in the experimental cell. The cell was flooded with electrolyte (H$_2$SO$_4$, sp.gr. 1.28), left to soak for 30 min and the free electrolyte was removed. A recombination electrode enveloped in poly(vinylchloride) (PVC) separator was mounted above the plates of the cell;

(iii) similar to (ii) above, but the WC electrode was wrapped in glass mat and impregnated with sulfuric acid. Every 8 h the glass-mat separator was wetted with 3 cm^3 of water to prevent the WC electrode from drying;

(iv) the experimental cell was a gelled-electrolyte battery cell. One-fifth of the WC recombination electrode, without PVC separator, was inserted in the gelled electrolyte with no contact with the battery plates;

(v) a dry WC electrode was placed in an experimental cell without electrolyte. In this case the gas mixture was fed in at a flow rate of 5000 cm^3 h^{-1}.

In the experimental setups described in (ii), (iv) and (v), a thermocouple was used for measuring the temperature at the surface of the WC electrode.

The recombination rate of hydrogen and oxygen on the WC electrodes was evaluated from the difference between the amounts of gas mixtures going into and out of the experimental cell.

Results

Figure 1 shows the time dependence of the recombination rate of WC electrodes under various operating conditions.
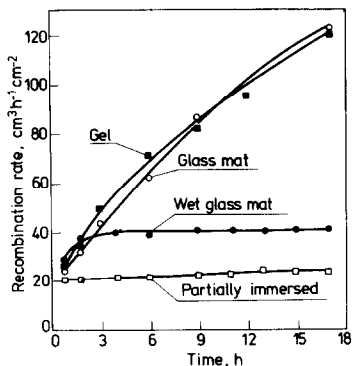
Fig. 1. The recombination rate of tungsten carbide electrodes as a function of the time of gas purging.

When WC electrodes are partially immersed in the electrolyte, a constant rate of hydrogen and oxygen recombination of about 20 cm^3 h^{-1} cm^{-2} is reached in the first hour of operation.

In the case of WC electrodes set in a battery cell with electrolyte immobilized in glass-mat separators, the recombination rate grows with time. This is due to the increase in temperature of the WC electrode as a result of the exothermal reaction of recombination. Under the above operating conditions (when 3700 cm^3 of gas mixture are fed per hour), a recombination rate of about 120 cm^3 h^{-1} cm^{-2} is reached after 17 to 18 h and the whole amount of gas fed in recombines on the WC electrode. The temperature of the WC electrode is about 80 to 85 °C and the electrode is apparently dry. On increasing the amount of gas mixture fed into the cell, the rate of recombination increases, and so does the electrode temperature, as under these conditions no heat exchange between the electrode and the electrolyte, respectively the experimental cell, is possible.

When WC electrodes are enveloped in a glass-mat separator and continuously moisturized, the recombination rate reaches a constant value relatively quickly, in about 3 h. This value of 40 cm^3 h^{-1} cm^{-2} is lower than that in the previous case but double the recombination rate of partially immersed WC electrodes. Wetting of the electrode by the glass mat prevents it from heating, and also probably leads to an increase in the reaction surface at the three-phase boundary, gas–liquid–catalyst, which facilitates the reaction of recombination.

For WC electrodes partially immersed in gelled electrolyte, the changes in recombination rate are similar to those for battery cells with glass-mat separators. Heating and drying of the recombination electrode is observed, and the recombination rate grows reaching a value of 120 cm^3 h^{-1} cm^{-2} in about 18 h at which time all of the gas mixture fed into the cell recombines to water. On reaching this recombination rate and at electrode temperature of about 80 °C, further increase in the gas mixture flow rate causes the electrode temperature to rise, because of the poor heat exchange between the WC electrode and the cell.

Based on temperature measurements carried out with WC electrodes in gelled and immobilized electrolytes, the temperature dependence of the recombination rate can be determined, and the activation energy of the recombination process be calculated.

The results obtained for temperatures ranging from 25 to 85 °C are presented in Fig. 2 in Arrhenius coordinates.

The energy estimated from this dependence, 20.93 kJ mol^{-1}, is very close in value to the activation energy of recombination of stoichiometric gas mixtures on partially immersed WC electrodes (15.49 kJ mol^{-1}) as established earlier [1]. This low value of the activation energy indicates that in the case of electrodes that are not in direct contact with the electrolyte, too, the rate-limiting stage in the recombination process is the impeded transport in the catalyzed electrode.

The results obtained from studying the performance of recombination electrodes in batteries with gelled or immobilized electrolyte pose the following two questions:

(i) How do WC recombination electrodes operate when they are not in contact with the electrolyte?

(ii) Is it possible that under these conditions water is formed on the WC electrode surface as a result of a chemical reaction between hydrogen and oxygen?

To answer these questions experiments were carried out with cells without electrolyte.

A WC electrode that had worked partially immersed in the electrolyte yielding a recombination rate of 20 cm^3 h^{-1} cm^{-2} was dried in the air and then inserted in the gas space of the experimental cell with no access to the electrolyte. The measurements were carried out by feeding stoichiometric hydrogen and oxygen gas mixture into the experimental cell at a flow rate of 7000 cm^3 h^{-1}. Figure 3 shows the changes in recombination rate and in electrode temperature under these conditions.

It can be seen from the Fig. that when using a dry WC electrode for gas recombination with no contact with the electrolyte, i.e., no heat exchange, in about 25 min the electrode temperature reaches the critical value of 100 °C, the rate of recombination being about 60 cm^3 h^{-1} cm^{-2} at that time. Then within 2 to 3 min, the rate of recombination increases rapidly up to 270 cm^3 h^{-1} cm^{-2}, and the electrode temperature reaches 340 °C. At this temperature, the H$_2$/O$_2$ mixture explodes. Numerous experiments have shown that every time the WC electrode is not able to exchange heat and the gas mixture is fed into the cell at a rate giving a recombination rate higher than 250 cm^3 h^{-1} cm^{-2}, the cell explodes after 25 to 30 min. This means that to prevent explosion of the battery cell containing WC recombination electrodes, the charging current should not exceed 300 mA per cm^2 of surface area of the built-in recombination electrode. In the above case, in which a single WC electrode is used
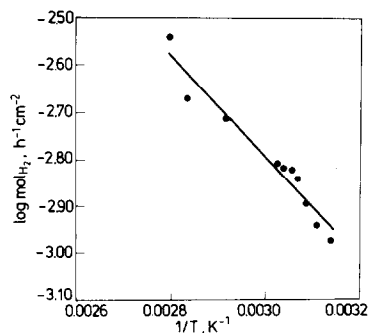

Fig. 2. Temperature dependence of the recombination rate of tungsten carbide electrodes.
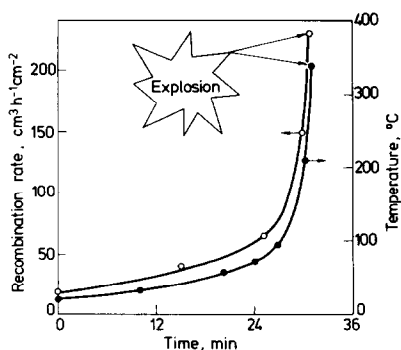
Fig. 3. Dependence of the recombination rate and the temperature of dry tungsten carbide electrodes on the time of gas purging.

with a surface area of 30 cm^2, the critical charging current which may cause explosion is 9 A. These experimental findings are in agreement with the test results obtained by Johnson Controls, Inc. [3].

To check the possibility of water formation through a chemical reaction a new dry WC electrode was used which had not been in contact with any electrolyte or water. The electrode was mounted in a dry experimental cell without electrolyte and subjected to further drying at 120 °C for 24 h. A gas mixture was fed into the cell from an electrolyser at a flow rate of 3700 cm^3 h^{-1}. To remove moisture from the gas mixture the latter was passed through a molecular sieve (Grace, type A4) and then fed into the cell containing the dry WC electrode. To avoid the effect of ingress of moisture from the surrounding medium all connections between the experimental cell, the electrolyser and the column were made of metal tubes. These measures were taken in order to allow the chemical reaction between the two gases:

$$2H_2 + O_2 \rightleftharpoons 2H_2O \tag{2}$$

to proceed at a maximum rate, i.e., to cause a shift of the equilibrium to the right. Subsequent measurements showed that under these conditions the rate of recombination of hydrogen and oxygen at the very beginning of gas mixture supply was 21.4 cm^3 h^{-1} cm^{-2}. This implies that a pure chemical reaction between the two gases is possible on the WC catalyst. If the new recombination electrode is soaked in water for 2 to 3 min before setting it in the dry cell, the initial recombination rate is about 8 cm^3 h^{-1} cm^{-2}. In this case, too, a chemical reaction proceeds but at a lower rate as the chemical equilibrium is shifted to the left. Obviously, the chemical and electrochemical reactions proceed in parallel on a partially immersed electrode. The rate of the electrochemical process may be assessed based on the potential/current characteristics of the investigated electrodes as recorded in the gas mixtures 66.6% H$_2$/33.3% Ar and 33.3% O$_2$/66.6% Ar, respectively (Fig. 4).

The current density at the intercept between the two curves can be used to calculate the rate of the electrochemical recombination which, in this case, is 14 cm^3 h^{-1} cm^{-2}. On grounds of the above results it can be concluded that in the case of partially immersed recombination electrodes the chemical and the electrochemical recombination processes occur at approximately the same rate.
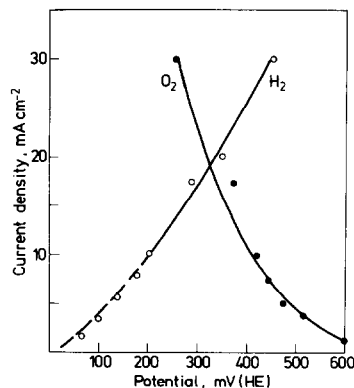

Fig. 4. Potential/current characteristics of partially immersed electrode; catalyst: 500 mg cm^2, temperature: 25 °C, H$_2$SO$_4$: sp.gr. 1.28.

Conclusions

The results obtained show that recombination WC electrodes can be used efficiently in sealed lead/acid batteries with gelled or immobilized electrolytes. These batteries exhibit a higher recombination rate compared to those with partially immersed WC electrodes due to heating of the recombination electrodes as a result of the exothermal reaction of recombination and the lack of heat exchange with the electrolyte and the cell. Hence, special measures should be taken to prevent explosion of the battery cells if the WC electrodes operate 'in a dry state'. The safety of the cells can be guaranteed by specifying a total surface area of the built-in recombination electrodes that ensures, under the optimum conditions of charge and overcharge, a rate of hydrogen and oxygen recombination not higher than 50–60 cm^3 h^{-1} cm^{-2}. On the other hand, the charging device should have an upper limit of the charging current and not allow overcharging with currents causing intense gassing that may result in an explosion.

References

1 I. Nikolov, G. Papazov, D. Pavlov, T. Vitanov and V. Najdenov, *J. Power Sources, 31* (1990) 69.
2 G. Papazov, I. Nikolov, D. Pavlov, T. Vitanov, P. Andreev and M. Bojinov, *J. Power Sources, 31* (1990) 79.
3 M. E. Taylor, T. Radojicic, J. S. Symanski and S. Kopf, *Techn. Rep., Nov. 1991*, Johnson Controls, Inc., Milwaukee, WI, USA.