

## SEALED LEAD/ACID BATTERY WITH AUXILIARY TUNGSTEN CARBIDE ELECTRODES

G. PAPAZOV\*, I. NIKOLOV, D. PAVLOV, T. VITANOV, P. ANDREEV and M. BOJINOV

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

---

### Introduction

In previous work [1], catalytic tungsten carbide (WC) electrodes were developed for the recombination of hydrogen and oxygen released during the operation of lead/acid batteries. These electrodes are mounted on the lid of each cell of a battery and are partially-immersed in the  $H_2SO_4$  solution. At room temperature, WC electrodes ensure effective chemical recombination between  $H_2$  and  $O_2$  when they are released in stoichiometric quantities.

During lead/acid battery operation, however, hydrogen and oxygen are very often evolved in a non-stoichiometric ratio. Combination of the over-stoichiometric gases can take place via an electrochemical reaction on the WC electrode proceeding in parallel with the chemical recombination between the two gases. To achieve this, a set of WC electrodes are connected to the positive battery plates and another set to the negative ones. To ensure adequate rates of reaction of hydrogen oxidation and oxygen reduction, the potential of the WC electrodes should be maintained within a particular range. Ruetschi and Ockermann [2], together with Shimizu and Okhawa [3], have suggested similar systems in which an auxiliary electrode catalyzed with platinum is connected by means of a diode to the lead plates of the cell. A second auxiliary electrode (also catalyzed with platinum) is connected to the  $PbO_2$  plates. In this case, however, platinum is partly dissolved in the electrolyte and deposition of platinum ions on the surface of the plates causes high rates of self-discharge and sulphation. These disadvantages, along with the high price of platinum, limit the application of such catalytic electrodes in lead/acid batteries. New catalysts for hydrogen oxidation and oxygen reduction based on tungsten carbide (WC) have been developed [1, 4, 5]. These catalysts overcome the shortcomings of the platinum catalysts to a considerable degree.

The aim of the present work is to investigate the performance of WC electrodes in two independent, self-controlled electrochemical cells where, in parallel with the recombination between hydrogen and oxygen, the reactions

---

\* Author to whom correspondence should be addressed.

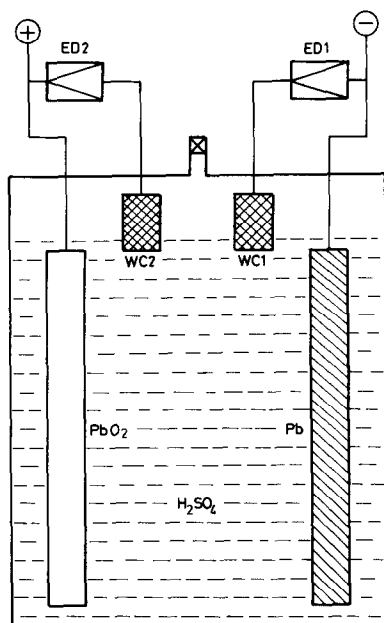


Fig. 1. Experimental lead/acid cell with auxiliary WC electrodes.

of hydrogen oxidation and of oxygen reduction also proceed. The operation of these two systems is examined during battery charge, discharge, overcharge, and on open circuit.

## Experimental

A schematic diagram of a lead/acid cell with two auxiliary WC electrode systems is given in Fig. 1. A set of three recombination electrodes is mounted in the lid of each cell. The technology for manufacture of the WC catalytic electrodes (consisting of tungsten carbide (WC), activated carbon (C) and carbon black) was discussed in refs. 1, 4 and 5. One WC electrode (WC1) was connected by means of an electronic device (ED1) to the negative plates of the cell in order to provide oxygen reduction. The remaining two auxiliary electrodes (WC2) were connected through an electronic device (ED2) to the positive plates for hydrogen oxidation. The lid was equipped with an outlet for measuring the gas pressure in the cell and with an outlet to a flowmeter which was switched on occasionally to measure the amount of unreacted gases.

ED1 is designed: (i) to maintain the potential of the WC1 electrode at +320 mV (*versus* hydrogen electrode) at which potential the recombination of  $H_2$  and  $O_2$  proceeds at a maximum rate, *i.e.*, the voltage drop on ED1 should be 650 mV; (ii) to allow electrons to move only from the lead to the WC1 electrode.

The function of the ED2 device is similar: (i) to maintain a potential of +320 mV on the WC2 electrodes, *i.e.*, the voltage drop on ED2 should be 1500 mV; (ii) to allow the electrons to flow only from the WC2 to the PbO<sub>2</sub> electrode.

The catalytic activity and the amounts of the electrode components, the technology for preparation of the porous mass, and the electrode construction are all important factors in minimizing the deviation of the potentials of the WC1 and WC2 electrodes from 320 mV during operation of the system.

The charge/discharge current and the voltage of the Pb/PbO<sub>2</sub> cell, as well as the currents of the WC1 and WC2 electrodes, were all measured continuously. The recombination efficiency of the catalytic WC electrodes was assessed by measuring the gas pressure and/or the amount of unreacted gases. The investigations were carried out at: (i) battery charge; (ii) overcharge and floating charge; (iii) discharge; (iv) open circuit.

## Results and discussion

### Battery charge

The cell was first fully charged and then discharged to 20% depth-of-discharge. After discharge, the cell was charged at 2 A, and the cell voltage and currents on the WC1 and WC2 electrodes were measured. The results are shown in Fig. 2. The behaviour of the WC electrode currents can be better understood by considering the reactions proceeding on the cell electrodes.

During charge, the current of the outer circuit (Fig. 1) is distributed in the cell as follows:

$$I = (I_{\text{Pb}} + I_{\text{H}_2})_{\text{Pb plate}} + (i_{\text{O}_2^-})_{\text{WC1}} \quad (1)$$

$$I = (I_{\text{PbO}_2} + I_{\text{O}_2})_{\text{PbO}_2 \text{ plate}} + (i_{\text{H}^+})_{\text{WC2}}$$

$I_{\text{Pb}}$  and  $I_{\text{PbO}_2}$  are the charge currents of the positive and negative plates;  $I_{\text{H}_2}$  and  $I_{\text{O}_2}$  are the currents of hydrogen and oxygen evolution and  $i_{\text{O}_2^-}$  and  $i_{\text{H}^+}$  are the oxygen reduction and hydrogen oxidation currents on the WC electrodes.

At the beginning of charge, since the overvoltages of hydrogen and oxygen on the Pb and PbO<sub>2</sub> electrodes are high:

$$I_{\text{H}_2} \longrightarrow 0 \quad I_{\text{O}_2} \longrightarrow 0. \quad (2)$$

To achieve effective charge:

$$(I_{\text{Pb}})_{\text{Pb plate}} \gg (i_{\text{O}_2^-})_{\text{WC1}} \quad (3)$$

$$(I_{\text{PbO}_2})_{\text{PbO}_2 \text{ plate}} \gg (i_{\text{H}^+})_{\text{WC2}} \quad (4)$$

This is obtained through the selection of suitable resistances in the electronic devices ED1 and ED2. Under this condition the entire current is utilized in charging the plates.

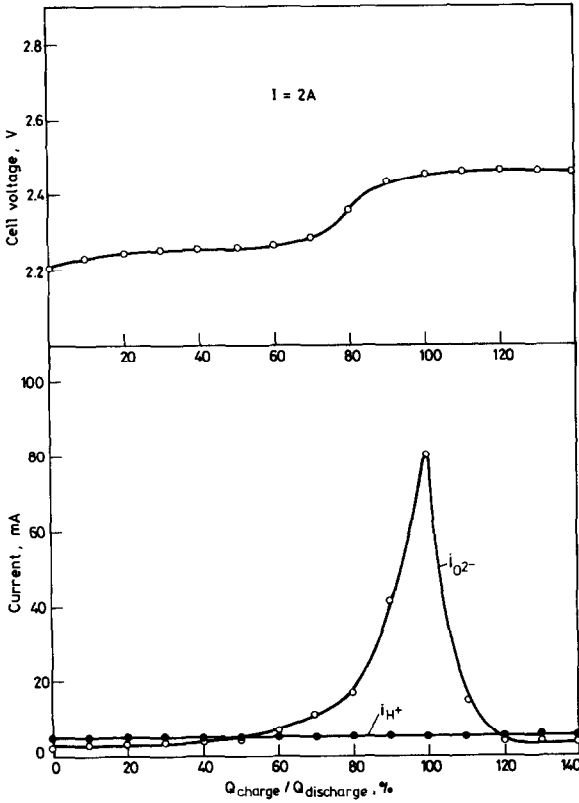


Fig. 2. Change in cell voltage and oxygen and hydrogen currents during charge.

When the positive plates reach 60 - 70% state-of-charge, oxygen evolution starts [6] and  $(I_{\text{O}_2})_{\text{PbO}_2 \text{ plate}} > 0$ . The total current,  $I$ , is distributed in the following way:

$$I = (I_{\text{PbO}_2} + I_{\text{O}_2})_{\text{PbO}_2 \text{ plate}} \quad (5)$$

$$I = (I_{\text{Pb}})_{\text{Pb plate}} + (i_{\text{O}_2^-})_{\text{WC1}} \quad (6)$$

It can be seen that  $(i_{\text{O}_2^-})_{\text{WC1}}$  is a function of the charge efficiency of the positive plate.

When the negative plate is charged to 95 - 100% state-of-charge, hydrogen is released and  $(I_{\text{H}_2})_{\text{Pb plate}} > 0$ . The total current will be distributed as follows:

$$I = (I_{\text{Pb}} + I_{\text{H}_2})_{\text{Pb plate}} + (i_{\text{O}_2^-})_{\text{WC1}} \quad (7)$$

The released hydrogen recombines with part of the oxygen on the WC1 and WC2 electrodes, whereby  $(i_{\text{H}^+})_{\text{WC2}}$  is still equal to zero. The total current in the  $\text{PbO}_2$  circuit remains:

$$I = (I_{\text{PbO}_2} + I_{\text{O}_2})_{\text{PbO}_2 \text{ plate}} \quad (8)$$

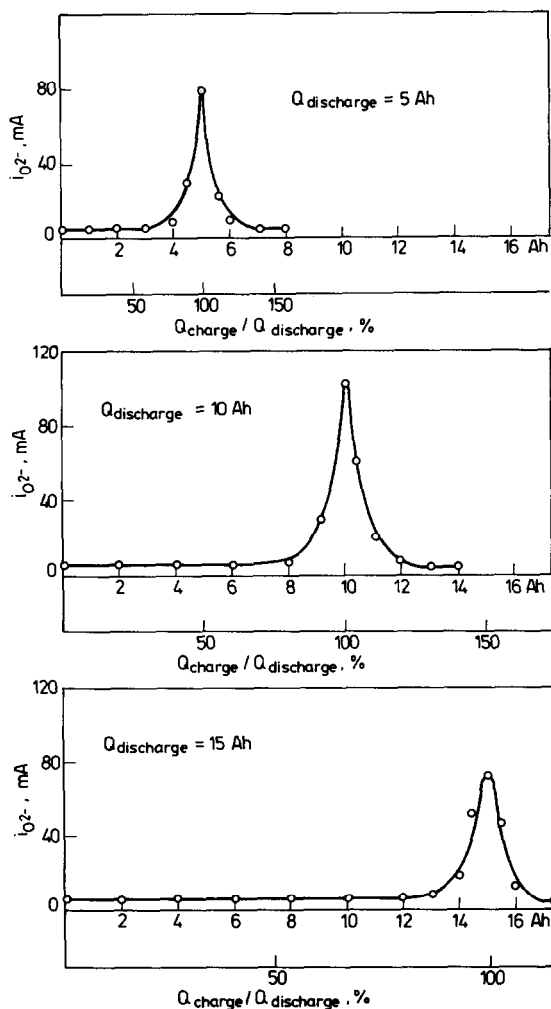


Fig. 3. Change in oxygen current during charging of a cell from different depths-of-discharge.

At full charge of the  $PbO_2$  and  $Pb$  plates, the charge currents become  $I_{Pb} \rightarrow 0$  and  $I_{PbO_2} \rightarrow 0$ . In this case,

$$I = (I_{H_2})_{Pb \text{ plate}} + (i_{O_2^-})_{WC1} \quad (9)$$

$$I = (I_{O_2})_{PbO_2 \text{ plate}} + (i_{H^+})_{WC2} \quad (10)$$

Figure 2 shows that after reaching full charge, the currents  $(i_{O_2^-})_{WC1}$  and  $(i_{H^+})_{WC2}$  are very low, while the charge current is 2.0 A. This indicates that the total amount of hydrogen and oxygen ( $1480 \text{ ml h}^{-1}$ ) is recombined on the WC1 and WC2 electrodes.

Analogous studies of the cell charge were carried out at different depths-of-discharge. Figure 3 gives the dependence of  $(i_{O_2^-})_{WC1}$  on the quantity

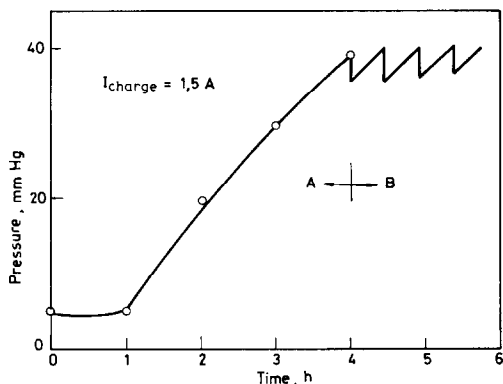


Fig. 4. Change in cell pressure during overcharge.

of charging electricity, as well as on the state-of-charge. It can be seen that, despite the different depths-of-discharge, a maximum in the  $(i_{\text{O}_2})_{\text{WC1}}$  circuit always appears at the end of charge. This phenomenon can find practical application in employing the WC electrode as a sensor to indicate the end of charge [7]. The signal obtained can be transmitted to the control unit of the charging device for a corresponding reaction.

### Overcharge

After charge, the lead/acid battery was subjected to overcharge at 1.5 A. The change in cell pressure with time was studied, see Fig. 4. Since the WC1 and WC2 electrodes can fully recombine the hydrogen and oxygen released at a current of 2.5 A, it is expected that the total amount of gas released at 1.5 A will be recombined and that the pressure during overcharge will remain constant. The results given in Fig. 4, however, indicate that there is a continuous increase in pressure over the interval A. Consequently, gas must have accumulated in the gas space; this is non-stoichiometric and causes an increase in pressure. A valve, functioning at a pressure of 40 mm mercury, was mounted on the lid of the cell. The pressure change in this case is presented by a curve within interval B. The oscillations are a result of switching the valve on and off.

It is necessary to determine the composition of the non-stoichiometric gas. For this purpose, the gas was fed into a separate electrochemical cell. The latter contained a WC electrode ( $1 \text{ cm}^2$ ) partially immersed in sulphuric acid solution and an  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference electrode. A measurement of the WC electrode potential was carried out. Nitrogen was first blown through the solution and the cell gas-space, after which the measurement was made. Figure 5 shows the change in the potential of the WC electrode with time. It can be seen that the potential quickly reaches the value of the hydrogen electrode potential. This shows that, during overcharge, over-stoichiometric hydrogen is accumulated in the cell. It was established that the gas is released at a rate equal to 1 - 1.5% of the overcharge current.

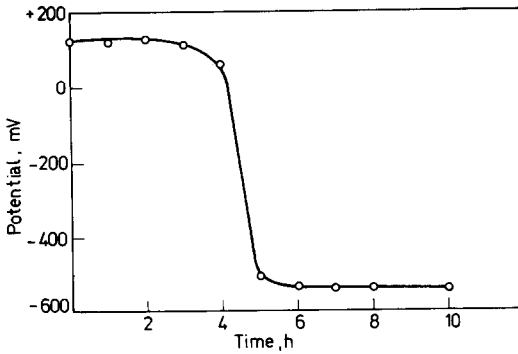


Fig. 5. Potential/time dependence of WC electrode during overcharge.

What is the reason for the formation of over-stoichiometric hydrogen? At overcharge, the currents flowing through the outer circuit are, respectively, equal to:

$$I = (I_{H_2})_{Pb \text{ plate}} + (i_{O_2^-})_{WC1} \quad (11)$$

$$I = (I_{O_2})_{PbO_2 \text{ plate}} + (i_{H^+})_{WC2} \quad (12)$$

Since  $(i_{O_2^-})_{WC1} \rightarrow 0$  and  $(i_{H^+})_{WC2} \rightarrow 0$ , it follows that during overcharge hydrogen and oxygen are released in the cell in stoichiometric amounts. Hence:

$$(I_{H_2})_{Pb \text{ plate}} = (I_{O_2})_{PbO_2 \text{ plate}} \quad (13)$$

Part of the released oxygen during overcharge takes part, however, in a grid corrosion process. It diffuses through the active mass and the corrosion layer, and then oxidizes the grid at a rate  $V_{corr}$  [8], according to:

$$(I_{O_2})_{PbO_2 \text{ plate}} = (V_{rec}/k)_{WC1 + WC2} + (V_{corr}/k)_{PbO_2 \text{ plate}} \quad (14)$$

where  $V_{rec}$  is the oxygen recombination rate of the WC1 and WC2 electrodes and  $k$  is a coefficient. Due to this grid corrosion process involving part of the released oxygen, an equivalent amount of hydrogen is not recombined. It is known [8] that the grid corrosion rate is equal to 1 or 2% of the oxygen evolution rate; the measured rate of hydrogen accumulation is in the same range.

It is interesting to discover whether the non-stoichiometric hydrogen can be recombined through an electrochemical reaction on the WC2 electrode. One possible method might be by decreasing the resistance of the ED2 electronic device whereby  $(i_{H^+})_{WC2} > 0$ . It follows from eqn. (12) that at a constant current in the outer circuit, any increase in the hydrogen current  $(i_{H^+})_{WC2}$  will bring about a corresponding decrease in the oxygen evolution current  $(I_{O_2})_{PbO_2 \text{ plate}}$ .

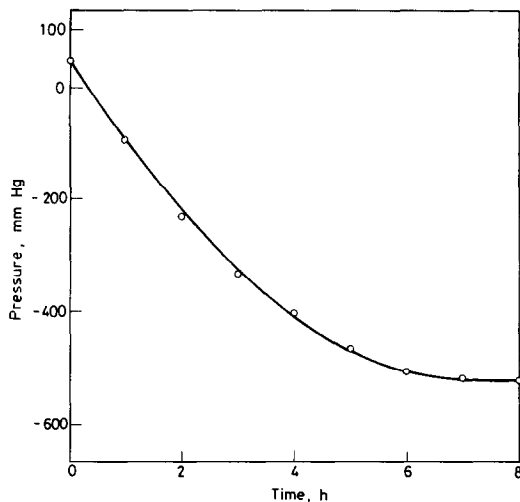


Fig. 6. Change in cell pressure during discharge.

The accumulation of hydrogen in the battery cell can be prevented by:

(i) mounting a valve that will open and release the gas when the pressure in the cell exceeds a pre-determined value; this will ensure very small water losses, depending on the corrosion rate;

(ii) interrupting the overcharge current for a definite period of time; during this period, a current flows between the WC2 and PbO<sub>2</sub> electrodes and oxidizes the hydrogen. Meanwhile, a very low positive plate discharge takes place.

Besides causing grid corrosion, oxygen may also oxidize the separator; this is accompanied by carbon dioxide release. In the studies reported here, there was negligible release of carbon dioxide.

### Discharge

A fully charged cell supplied with recombination electrodes was subjected to discharge at 4 A for 8 h. To avoid gas leakage, the cell was placed in a sealed chamber. The pressure change in the chamber and the hydrogen and oxygen currents ( $i_{O_2^-}$  and  $i_{H^+}$ ) flowing through the WC electrodes were measured. During discharge, no current changes were observed. The pressure changes are presented in Fig. 6.

After switching on the discharge current, hydrogen and oxygen evolution stops. A recombination of the gases released during discharge proceeds on the WC electrodes and the cell pressure starts to decrease. In 6 h, a high vacuum is obtained (below 600 mm mercury) which is maintained throughout the subsequent discharge.

The discharge currents of the positive ( $I_d^+$ ) and the negative ( $I_d^-$ ) plates can be expressed in terms of the discharge current in the outer circuit ( $I$ ) and



the oxygen and hydrogen currents, as follows:

$$I_d^+ = I + (i_{H^+})_{WC2} \quad (15)$$

$$I_d^- = I + (i_{O^{2-}})_{WC1} \quad (16)$$

In this case, the total amount of electricity ( $It$ ) flowing through the outer circuit will be determined by the difference between the plate capacity and the amount of electricity consumed for the electrochemical reactions of hydrogen oxidation and oxygen reduction, *i.e.*,

$$It = (I_d^+ - (i_{H^+})_{WC2})t \quad (17)$$

$$It = (I_d^- - (i_{O^{2-}})_{WC1})t \quad (18)$$

To obtain negligible capacity losses,  $(i_{H^+})_{WC2}$  and  $(i_{O^{2-}})_{WC1}$  should be very low, *i.e.*, the electronic devices should have high resistances. The vacuum formed during discharge is higher than the battery case can withstand. On the other hand, it was established that vacuum decreases the catalytic activity of the WC electrodes by 50 - 60%, due to filling of the microporous catalytic mass with water and electrolyte. This requires the use of a safety valve that will let air into the cell when a pre-determined value of the vacuum is reached (up to 30 - 40 mm mercury).

### Open circuit

When the charge current is switched off, hydrogen and oxygen evolution stops and a process of recombination starts. The pressure changes in the cell are similar to those occurring on discharge (Fig. 6). In this case, the above requirements for the prevention of high vacuum formation are also valid.

Since  $I = 0$  at open circuit,  $(i_{O^{2-}})_{WC1}$  and  $(i_{H^+})_{WC2}$  are the discharge currents of the corresponding plates:

$$I_d^- = (i_{O^{2-}})_{WC1} \quad (19)$$

$$I_d^+ = (i_{H^+})_{WC2} \quad (20)$$

It can be assumed that this is self-discharge since there is no current flowing through the outer circuit. To obtain low discharge, the currents  $i_{O^{2-}}$  and  $i_{H^+}$  should be very low.

At open-circuit, self-discharge takes place in the battery cell giving rise to release of hydrogen. To determine the changes in the gas phase and the amount of released hydrogen, the gases from a cell without WC recombination electrodes were directed to the measuring electrochemical cell and then to a flowmeter. The potential changes of the WC electrode in the above cell after opening the circuit are presented in Fig. 7. These results show that hydrogen accumulates during self-discharge at a rate of 30 - 60 ml h<sup>-1</sup>. For the electrochemical oxidation of this hydrogen, a current of up to 100 mA is needed. This imposes the following important requirement on the electronic device: when the gas phase contains over-stoichiometric hydrogen and the WC electrode potential is shifted in the direction of the hydrogen potential, the device current should be sufficient for the electrochemical oxidation of the

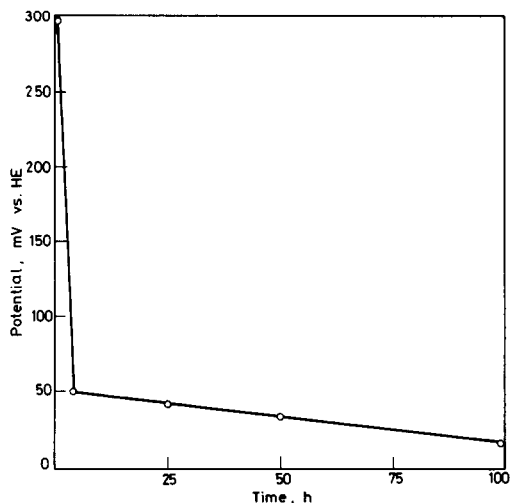


Fig. 7. Potential/time dependence of WC electrode at open circuit.

over-stoichiometric hydrogen. This current will cause additional self-discharge of the positive plates.

## Conclusions

Results show that a self-controlled, sealed system can be developed for a lead/acid battery cell by using partially-immersed electrodes containing a mixture of WC and C as catalysts, and a safety valve mounted in the battery lid. The electrodes are connected by means of electronic devices to the positive and negative battery plates. This system allows the battery to operate without any water loss, and is especially suitable for use in stationary batteries and load-levelling systems where water maintenance is a major problem during battery service life.

## References

- 1 I. Nikolov, G. Papazov, D. Pavlov, T. Vitanov and V. Naidenov, *J. Power Sources*, 31 (1990) 69.
- 2 P. Ruetschi and J. Ockerman, *Electrochem. Technol.*, 4 (1966) 383.
- 3 K. Shimizu and Y. Ohkawa, in Y. Miyake and A. Kozawa (eds.), *Rechargeable Batteries in Japan*, JES Press Inc., 1977, p. 257.
- 4 I. Nikolov, V. Nikolova and T. Vitanov, *J. Power Sources*, 4 (1979) 65.
- 5 I. Nikolov, V. Nikolova and T. Vitanov, *J. Power Sources*, 7 (1981/82) 83.
- 6 K. Peters, A. I. Harrison and W. H. Durant, in D. H. Collins (ed.), *Power Sources 2*, Pergamon Press, Oxford, 1968, p. 1.
- 7 *Bulg. Pat.* 73,149.
- 8 D. Pavlov and T. Rogatchev, *Werkst. Korros.*, 19 (1968) 677.