Journal of Power Sources, 40 (1992) 175–186

Noble metal-free catalysts for the hydrogen/oxygen recombination in sealed lead/acid batteries using immobilized electrolytes

H. Dietz, L. Dittmar, D. Ohms, M. Radwan and K. Wiesener
Dresden University of Technology, Institute of Physical Chemistry and Electrochemistry, Mommsenstrasse 13, D(O)-8027 Dresden (Germany)

Abstract

In order to remove hydrogen in sealed lead/acid batteries operating on oxygen cycle the facility to recombine hydrogen and oxygen at a catalyst in the gas phase was studied. Based on the assumption of an electrochemical mechanism, several catalytic materials were investigated. It has been shown that noble metal-free composite materials based on tungsten carbide (WC) and carbon can be applied as catalysts for this purpose. The working conditions for their application in model cells were discussed. The efficiency of such catalysts in sealed lead/acid batteries was also demonstrated.

Introduction

Influenced by the intensive development of electrotechniques and electronics, nowadays a wide range of market sectors requires sealed lead/acid batteries.

A major problem of sealed lead/acid batteries is the control of the gas pressure. Whereas the efficiency of the oxygen cycle in sealed lead/acid batteries is close to 100%, an analogous hydrogen cycle cannot be achieved, as the hydrogen oxidation is kinetically hindered at the working potential of the positive electrode.

Therefore, in sealed lead/acid batteries: (i) the hydrogen evolution is usually suppressed (by charging at low constant voltage, using cell components of high purity, especially antimony-free lead alloys etc.); (ii) evolved hydrogen can be oxidized, e.g., electrochemically at (catalyzed) auxiliary electrodes or by currentless catalytic hydrogen/oxygen recombination, and (iii) excess hydrogen is removed by means of a safety-valve together with oxygen.

The catalytic recombination principle has been frequently proposed for lead/acid batteries with flooded electrolyte:

(a) as catalytic plug for the hydrogen/oxygen recombination in order to achieve maintenance-free operation [1], and
(b) in combination with auxiliary electrodes held at special potentials (by means of diodes connected to the battery electrodes) to insure oxygen reduction or hydrogen oxidation [2].

As gas evolution does not proceed stoichiometrically, the gas recombination principle (a) cannot be used as a unique recombination method in sealed batteries. Compared to it, the mixed principle (b) even seems to allow a hermetically-sealed construction [2].

0378-7753/92/$5.00 © 1992 – Elsevier Sequoia. All rights reserved

However, there are some obstacles that have not allowed industrial application on a large scale yet. These are the complicated voltage control measures and the disadvantages involved in the application of noble metal catalysts (high costs, expensive precautions against poisening of the catalyst [3], and explosion hazards at high reaction yields [1, 3], risk of increasing self-discharge by the decrease of the hydrogen overpotential caused by noble metal traces in the electrolyte).

On the other side, recent experiments have clearly demonstrated that also noble metal-free catalysts based on tungsten carbide (WC) [4] can be applied to recombine excess gases in sealed lead/acid batteries efficiently [5–8], thus confirming previous results [9].

As pointed out by Nikolov *et al.* [6], WC-carbon electrodes additionally installed and partly immersed in H_2SO_4 solution are found to be long-term active and to allow maintenance-free operation of stationary lead/acid batteries under float conditions. The same catalytic electrodes connected to the battery plates by means of electronic devices are proposed according to the mixed principle (b) for use in sealed batteries under stationary and load-leveling conditions [7].

The importance of the hydrogen/oxygen recombination catalysis, however, is not restricted to flooded batteries. Sealed types are utilizing mainly immobilized electrolytes, thus enabling an efficient oxygen cycle.

In order to remove excess hydrogen the hydrogen/oxygen recombination catalysis at a catalyst in the gas phase should be applied as an additional measure to the oxygen cycle.

It is well known that the currentless hydrogen/oxygen recombination includes partial reaction steps with radicals and ions. Thus, these reactions can be considered as electrochemical reactions. As a consequence, the catalyst should be a composite consisting of components for both the hydrogen oxidation and oxygen reduction. It should have sufficient electrical conductivity or should be precipitated onto a conductive support, e.g., WC on active carbons.

From the literature, only sparse information is available on composition, mechanism and optimal working conditions of noble metal-free catalysts located in the gas space of sealed lead/acid batteries using immobilized electrolytes [6, 12].

The aim of this paper is therefore:

(i) to characterize the activity of gas space catalysts for hydrogen/oxygen recombination in the absence of gas-consuming battery electrodes in dependence on activating parameters like catalyst composition, gas medium, etc., and

(ii) to investigate the efficiency of a suitable composite catalyst in sealed lead/acid batteries operating on the oxygen cycle.

Experimental

Various composite materials (WC-*X*) bound by polytetrafluoroethylene (PTFE) were pressed to form tablets and used as catalysts in model cells.

Type and concentration of the oxygen reduction component *X* were varied using a constant amount of WC. As components for the oxygen reduction catalysis the following materials *X* were investigated: (i) active carbon P33, (ii) acetylene black P1250, (iii) dibenzotetraazaannulene cobalt(II) (CoTAA) heat-treated at carbon P33, and (iv) cobalt acetate/polyacrylonitrile (CoAc–PAN) precipitated and heat-treated at active carbon.

Preparation and properties of the materials under investigation are described elsewhere [10–13].

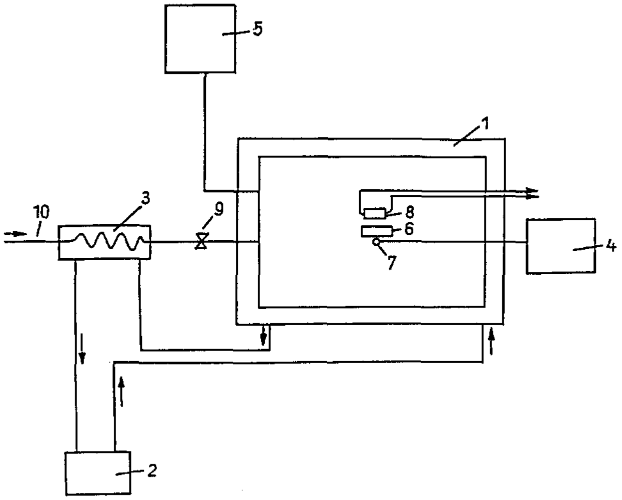


Fig. 1. Equipment for calorimetric measurements of the heat flow at the surface of gas-space catalysts for the hydrogen/oxygen recombination: (1) double-wall glass tube; (2) thermostat; (3) prethermostat; (4) temperature recorder; (5) pressure monitor; (6) catalyst pellet; (7) temperature sensor; (8) filament for calibration; (9) valve, and (10) gas inlet.

Besides polarization measurements at gas-fed electrodes made of catalyst materials, mainly the activity of gas space catalysts were investigated using: (i) pressure decay curves in gas-tight model cells after generation of a stoichiometric hydrogen/oxygen gas mixture by electrolysis of H_2SO_4 solution at grids made of pure lead, and (ii) calorimetric measurements (heat flow at the surface of catalysts) using temperature sensors in thermostated cells after infeeding a hydrogen/oxygen gas mixture until 45 kPa. For calibration, a filament resistance in the same position as the catalyst was used (Fig. 1).

Results and discussion

Investigations without gas-consuming battery electrodes

Catalyst type

In Fig. 2, the influence of noble metal and noble metal-free composite material on overpressure versus time curves is shown. Although the WC-carbon catalyst demonstrates lower activity than platinum, a promising rate of pressure decay is obtained. Increasing the amount of catalyst in the composite material is expected to make it competitive with the platinum material, as pointed out in [6].

In Fig. 3, polarization curves of gas-fed electrodes made of WC and carbon with PTFE binder in H_2SO_4 solution are visualized. The potential range of application is limited to values lower than 500 mV versus RHE. Above this value the efficiency of the anodic hydrogen oxidation is decreased (curve 1 and 1′) and the material is oxidized (curve 3). Above this value the electrode material (WC and/or carbon) is oxidized (curve 3). Thus, it can be concluded, that (i) the mixed potential of a WC-C-composite in the gas space must not exceed 500 mV to prevent partial oxidation and deactivation of the catalyst, and (ii) the composite catalyst should contain an oxygen catalyst of only moderate activity in low concentration.

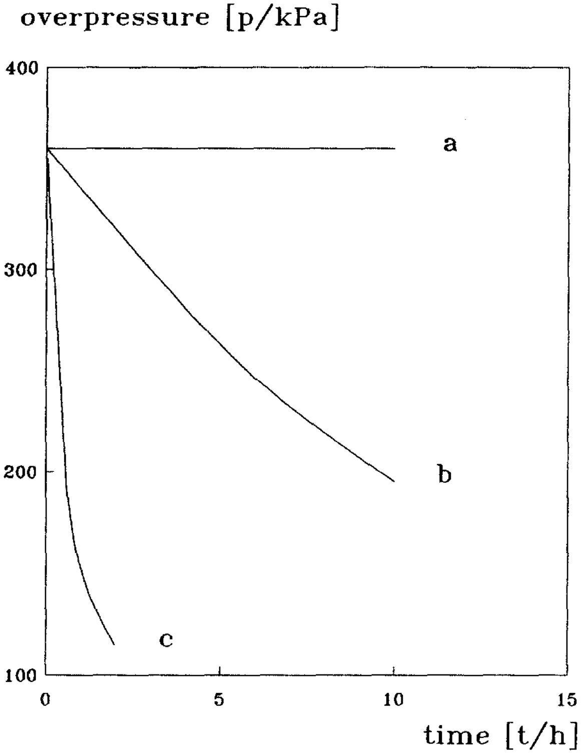


Fig. 2. Pressure decay curves of the hydrogen/oxygen recombination at different gas-space catalysts in gas-tight cells without gas-consuming electrodes: (a) without catalyst; (b) with 0.2 g (15% WC, active carbon P33 and 15 wt.% PTFE), and (c) with 0.2 g (0.25 wt.% Pt on active carbon P33 and 15 wt.% PTFE).

Catalyst composition

It is known from the literature that also WC itself is somewhat active with respect to oxygen reduction and its activity towards both hydrogen oxidation and oxygen reduction is substantially increased by adding active carbon [6]. One reason for this is assumed to be the improved gas transport in the reaction layer. Our measurements with gas-fed electrodes confirm these findings (Fig. 4). Due to the increase of the surface area of carbon, and consequently finely-dispersed WC, the electrocatalytic action is enhanced. The studies show further that increasing action of the oxygen-reduction component of the catalyst results in a shift of the mixed potential to the anodic direction (Fig. 4(b) and (c)). This illustrates the risk of partial oxidation of WC to lesser active tungsten oxides in the case of the presence of active oxygen, if reduction catalysts like heat-treated macrocycles (e.g., CoTAA) are used (Fig. 4(c)). As seen from Fig. 4(c), after long-term polarization the activity for oxygen reduction is decreased, which may be explained by instantaneous depletion of oxygen at the three-phase boundary.

The equipment according to Fig. 1. was used to compare the activity of different gas-space catalysts calorimetrically. The temperature measurements were carried out 500 s after infeeding a hydrogen/oxygen mixture into the calorimeter. In Fig. 5, the heat flow for the recombination of hydrogen and oxygen at a variety of catalytic

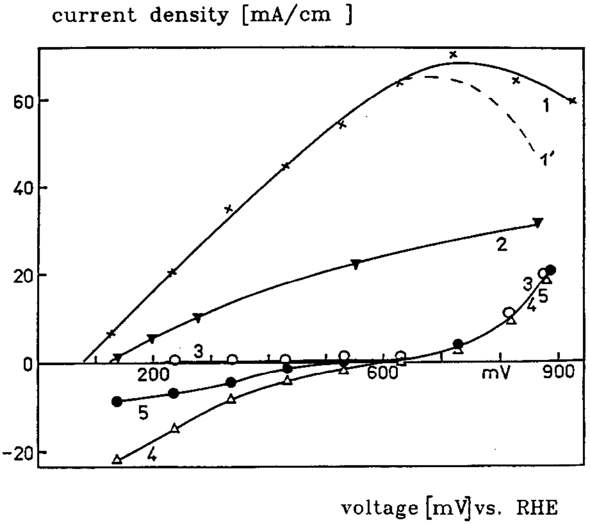


Fig. 3. Polarization curves at gas-fed electrodes made of the catalyst material obtained in sulfuric acid solution (sp. gr. 1.28) at a pressure of 101 kPa (88.7wt.%WC–2.2wt.%P33–4.3wt.%P1250–4.8wt.%PTFE): (1) H_2(101 kPa); (2) H_2(10 kPa)–N_2; (3) N_2(101 kPa); (4) O_2(101 kPa), and (5) O_2(10 kPa)–N_2.

materials is shown. With increasing amount of PTFE the activity of the material decreases, as active centres for hydrogen/oxygen recombination (Fig. 5(a)) were blocked. In the case of the use of dry catalysts no substantial influence of the amount of active carbon can be observed (Fig. 5(b)). A possible dependence, however, may be covered by simultaneous alteration in the heat capacity.

Moistening

As seen from Fig. 5, moistening of catalysts increases its catalytic activity. In particular, this becomes more visible when composite catalysts are used (Fig. 5(b), Fig. 9) rather than in the case of WC–PTFE without additional oxygen-reducing components (Fig. 5(a)). With increasing immersion in water activation continues; in some cases the activity is enhanced by up to 500%. It should be mentioned that during immersion of WC in water its surface area changes its colour, similar to what occurs during drying. Hence, it can be concluded that highly-active W–O compounds were formed. It was found that the activation depends mainly upon the duration of moistening rather than the rate of immersion.

Two explanations can be taken into consideration: (i) a chemical mechanism of the recombination, e.g., disproportionation of tungsten of WC and/or, in particular, and (ii) an electrochemical mechanism which supposes the presence of electrolyte phases.

The latter assumption is favoured because the mixed potential depends upon the gas composition as shown in ref. 10 and wetting as well as electrical conductivity of the support leads to an increased rate of recombination.

Further studies are necessary for a complete understanding of this matter.

Gas composition

Pressure versus time curves due to hydrogen/oxygen recombination in model cells (Fig. 6) show that: (i) the WC–active carbon composite catalyst under investigation

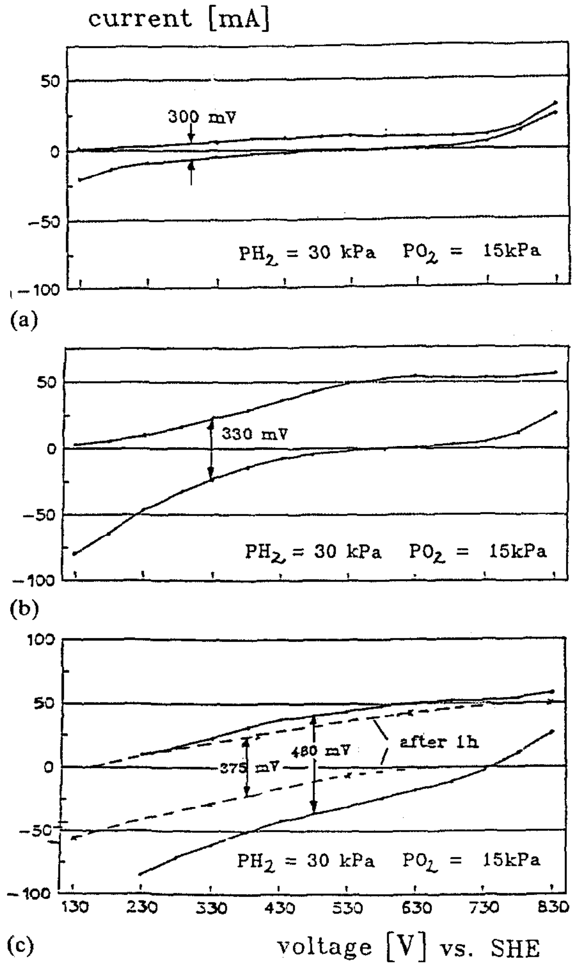


Fig. 4. Polarization characteristics of gas-fed electrodes made of 355 mg WC–5wt.%PTFE: (a) without additional oxygen reduction component; (b) with additionally 5% active carbon P33, and (c) with additionally 5% active carbon + 0.9% CoTAA, heat-treated.

is able to recombine hydrogen/oxygen mixtures completely; (ii) excess oxygen does not improve hydrogen/oxygen recombination, and (iii) excess hydrogen increases the ability to recombine hydrogen/oxygen mixtures.

Moreover, calorimetric measurements at constant total pressure show (Fig. 7) that the recombination rate is the highest at the stoichiometric gas composition, thus confirming recent results from the literature [6].

A certain influence of the prestorage gas medium on the initial activity of the composite catalyst can also be observed (Fig. 8). Whereas storage under hydrogen results in an initial temperature maximum for the recombination, the initial activity of catalyst storaged under oxygen is very low. This effect correlates with results from Fig. 6 and should be explained by the oxygen content at the surface of the catalyst. The further course of the curve shows that the initial influence of the storage gas is

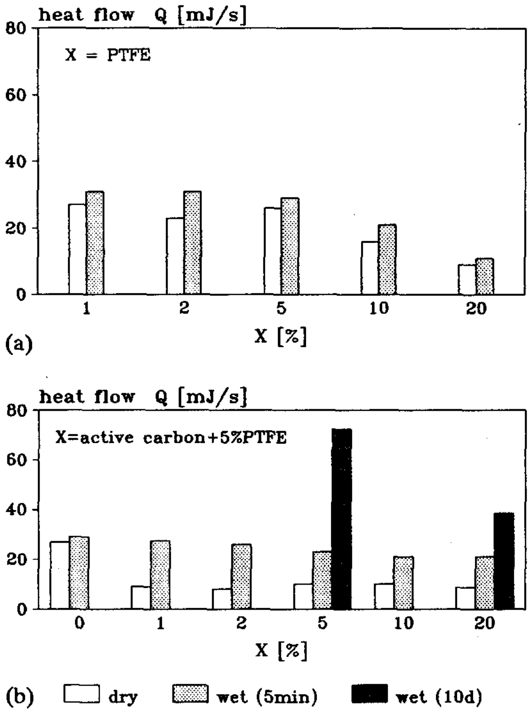


Fig. 5. Activity of some catalysts (355 mg WC–*X*) for recombination of a stoichiometric hydrogen/oxygen gas mixture (p(H_2): 30 kPa, p(O_2): 15 kPa, p(N_2): 101 kPa) in dependence on catalyst composition *X* and immersion time of the catalyst in water; (a): *X* = PTFE, and (b) = active carbon + 5 wt.% PTFE.

neutralized with increasing time. This indicates the reversibility of the coverage of oxygen species. A special prestorage in a special gas atmosphere does therefore not appear to be necessary.

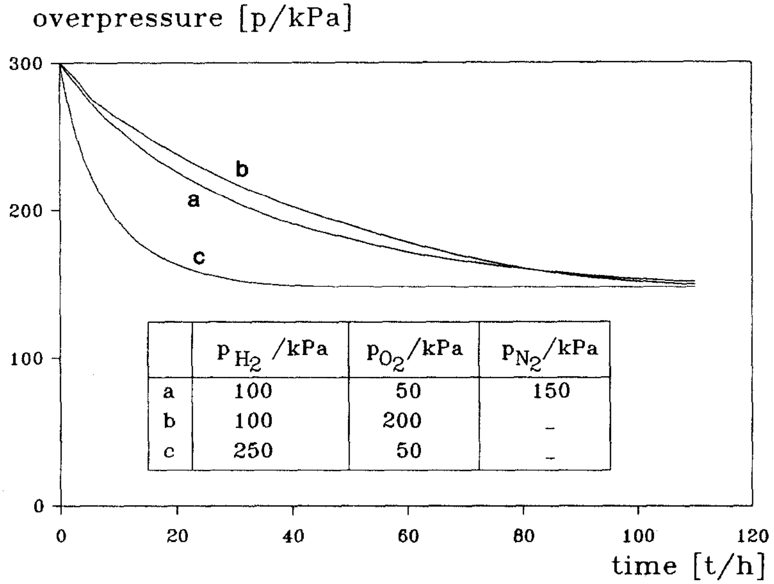
Component for oxygen reduction

In Fig. 9, an overview of the calorimetric activity of various composite catalysts is given. It become obvious on it that (i) WC–PTFE catalysts have little activity if compared to composite catalysts with an additional oxygen-reduction component, as WC is only a poor oxygen catalyst, and (ii) an additional oxygen reduction catalyst such as active carbon increases the activity, but more active oxygen-reduction catalysts (CoAC–PAN) are not necessary or they increase the risk of partial oxidation of WC, especially at high yields and high pressure of oxygen (e.g. CoTAA, see also Fig. 5(c)).

Investigation of sealed batteries operating on the oxygen cycle

To study the effect of gas-space catalysts for hydrogen/oxygen recombination in sealed lead/acid batteries with immobilized electrolytes, overpressure versus time curves were recorded during overcharging and cycling. A composite catalyst WC mixed with carbon P33 and P1250 was used.

Our results show that this catalyst is able to remove hydrogen almost completely during overcharging, i.e., the H_2 pressure is decreased by 10 to 30%, depending on



	p_{H_2} /kPa	p_{O_2}/kPa	p_{N_2}/kPa
a	100	50	150
b	100	200	-
c	250	50	-

Fig. 6. Pressure decay curves for the hydrogen/oxygen recombination at composite catalysts made of tablets (0.2 g) of (88.7wt.%WC–2.2wt.%P33–4.3wt.%P1250–4.8wt.%PTFE) depending on the gas composition: (a) stoichiometric hydrogen/oxygen mixture; (b) excess oxygen, and (c) excess hydrogen.

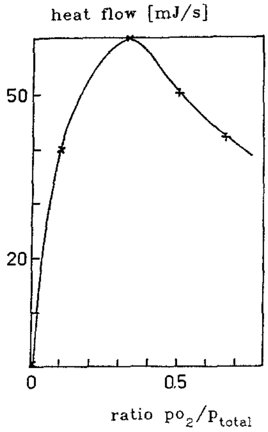


Fig. 7. Activity (measured as heat flow) of a recombination catalyst depending on the oxygen content at constant total pressure; catalyst composition: 0.355 g WC–5wt.%P33–2wt.%CoAc–PAN (heat-treated on the carbon)–5wt.%PTFE.

polarization and H_2 overvoltage at the negative electrode. Even in the absence of antimony and at low polarization of 2.30 V the H_2 pressure is lowered to less than 25% (Fig. 10).

The high efficiency of the catalyst is mainly seen during cycling, as in sealed cells H_2 accumulation takes place.

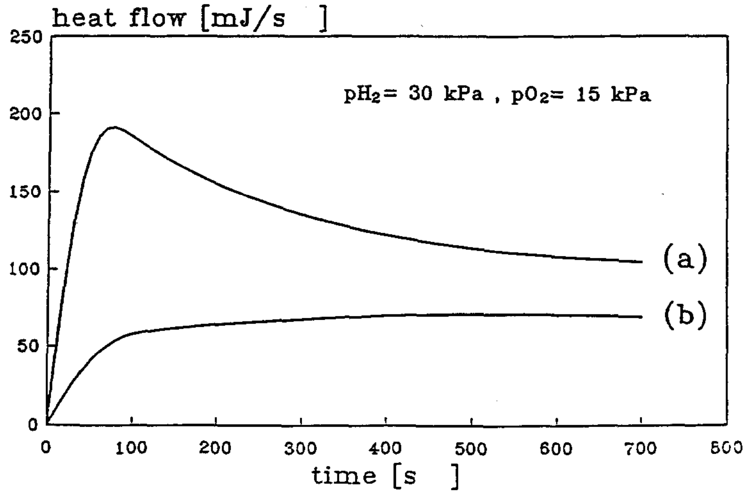


Fig. 8. Activity of a hydrogen/oxygen recombination catalyst depending upon a prestorage in different gases, with catalyst composition: 0.355 g WC–5wt.%P33–2wt.%CoAc–PAN (heat-treated on the carbon)–5wt.%PTFE: (a) stored under hydrogen, and (b) stored under oxygen.

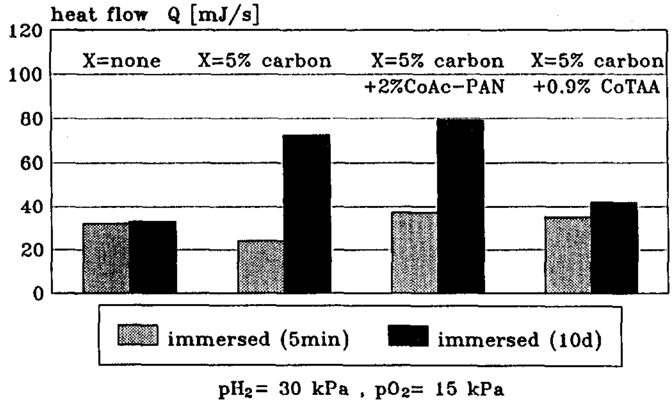


Fig. 9. Activity of various composite catalysts made of 0.355 g WC–5wt.%PTFE–*X* in dependence on the type of the oxygen reduction component *X*.

The catalyst is efficient enough to overcompensate the antimony poisoning effect caused by using Pb–2.5wt.%Sb grid alloys instead of antimony-free materials (Fig. 11).

These examples show that the efficiency of the catalyst (ratio of consumed to formed hydrogen) increases if the rate of H_2 evolution is enhanced (use of Pb–Sb alloys, high-overcharging currents, poor O_2 recombination efficiency, etc.).

In Fig. 12 the efficiency of the gas-space catalyst in sealed batteries using absorptive separators which were completely saturated by electrolyte is shown. To prevent higher pressure values than 40 kPa the cell was vented after reaching this limit. On applying 2 V/5.5 A h batteries and the given cycling regime (50% DOD, 2.35 V charging

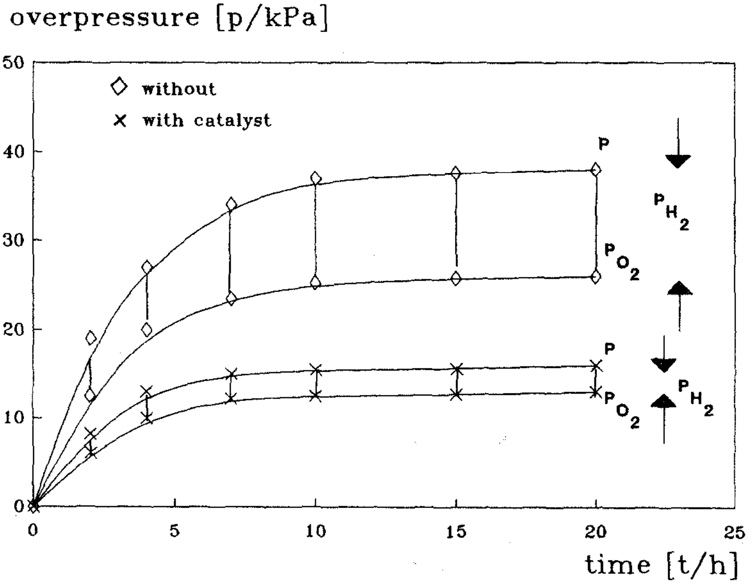


Fig. 10. Influence of a hydrogen/oxygen recombination catalyst on pressure course during overcharging at 2.30 V of a sealed lead/acid cell (2 V, 5.5 A h) using an absorptive separator (100% saturated); catalyst: 0.4 g (88.7wt.%WC–2.2wt.%P33–4.3wt.%P1250–4.8wt.%PTFE).

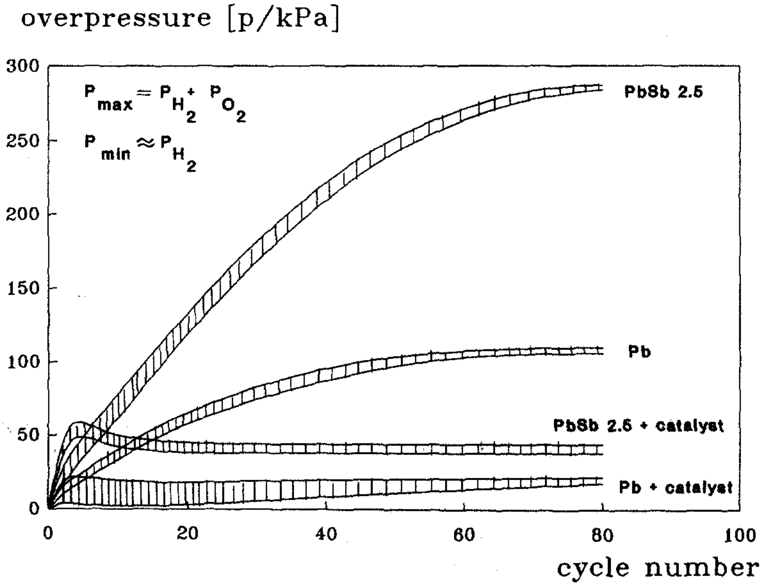


Fig. 11. Influence of a hydrogen/oxygen recombination catalyst on pressure course during cycling of sealed lead/acid cell (2 V, 3 A h) using 60 g gelled electrolyte; catalyst: 0.4 g (88.7wt.%WC–2.2wt.%P33–4.3wt.%P1250–4.8wt.%PTFE); cycling regime discharge current: 0.170 C_{20}/h for 3 h and charge current: 0.065 C_{20}/h for 9 h.

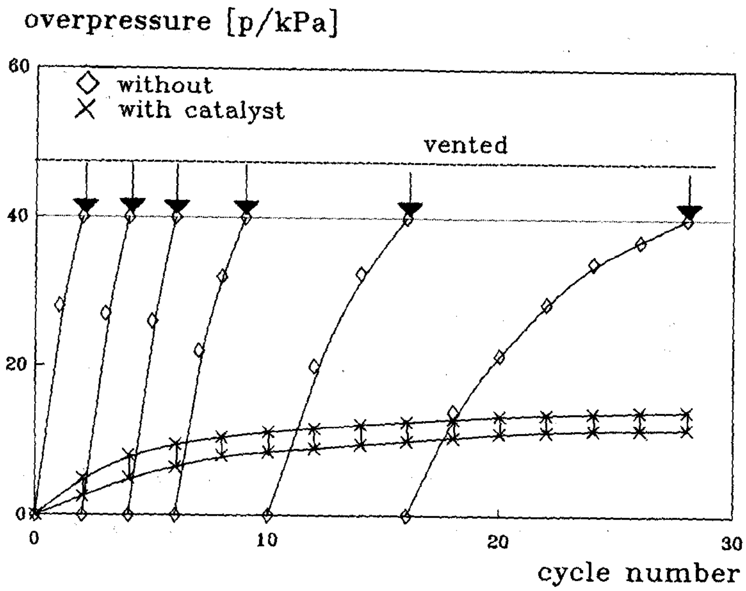


Fig. 12. Influence of hydrogen/oxygen recombination catalyst on pressure course during cycling of sealed lead/acid cells (2 V, 5.5 A h) using an absorptive separator (100% saturated); catalyst: 0.4 g (88.7wt.%WC–2.2wt.%P33–4.3wt.%P1250–4.8wt.%PTFE); cycling regime discharge current: 0.170 C_{20}/h for 3 h and charging voltage: 2.35 V for 9 h.

voltage) the catalyst enables the cell pressure to achieve stationary values at approximately 10 kPa.

The results suggest that the use of catalysts for hydrogen/oxygen recombinations not only of importance for sealed batteries using a safety valve but also for the idea of constructing hermetically-sealed lead/acid batteries. For the latter, a requirement to be fulfilled consists in achieving a maximum pressures of less than about 10 kPa over the operational life of the battery.

Conclusions

In order to remove hydrogen in sealed lead/acid batteries operating on the oxygen cycle, the method to catalyze hydrogen/oxygen recombination in the gas space seems to be suitable. Assuming that this catalytic reaction is a chemical process including electrochemical partial steps, the catalyst should be a composite material capable of catalyzing both the anodic hydrogen oxidation as well as the cathodic oxygen reduction. It should have sufficient intrinsic conductivity and chemical and electrochemical stability. Catalysts from fuel-cell investigations in acid electrolytes were considered to be suitable substances. Thus specially-prepared WC precipitated on a high-surface-area carbon was investigated. From reasons of chemical and electrochemical stability, the mixed potential of this catalyst in the gas mixtures in a sealed battery must not exceed 500 mV versus RHE in order to prevent partial oxidation of WC. Therefore, the component for oxygen reduction should have a moderate activity only.

The activity of the composite catalysts installed inside the gas space of sealed cells depends on its composition, moisture content, gas pressure and composition. This emphasizes the electrochemical steps involved in the chemical recombination of hydrogen/oxygen mixtures. The low value of the resulting cell pressure in laboratory test cells during overcharging and cycling confirms the high efficiency of the catalyst mentioned above. Its efficiency in sealed lead/acid batteries increases with raising hydrogen content depending on the type of the grid alloy, oxygen cycle efficiency and test regime.

References

1 K. Ledjeff and A. Winsel, *J. Power Sources, 8* (1982) 211.
2 P. Ruetschi and J. B. Ockerman, *Electrochem. Technol., 4* (1966) 383.
3 J. I. Dyson and E. Sundberg, in D. H. Collins (ed.), *Power Sources 4,* Academic Press, Newcastle, 1973, p. 305.
4 H. Bohm, *Electrochim. Acta, 15* (1970) 1273.
5 K. Berthold, *Thesis*, University of Technology, Dresden, 1987.
6 I. Nikolov, G. Papazov, V. Naidenov, T. Vitanov and D. Pavlov, *J. Power Sources, 31* (1990) 69.
7 G. Papazov, I. Nikolov, D. Pavlov, T. Vitanov and P. Andreev, *J. Power Sources, 31* (1990) 79.
8 H. Dietz, S. Voss, H. Döring, J. Garche and K. Wiesener, *J. Power Sources, 31* (1990) 107.
9 M. Jung, *Ger. Patent DE 2 312 131* (1973).
10 D. Ohms, L. Dittmar, H. Dietz and K. Wiesener, *Chem. Tech., 43* (5) (1991) 187.
11 N. D. Hung, S. Rudolf, O. Rademacher and K. Wiesener, *Z. Chem., 16* (1976) 30.
12 D. Ohms, W. Schneider, K.-H. Ulbricht and K. Wiesener, *Z. Phys. Chem., (Leipzig) 267* (1986) 45.
13 R. Franke, D. Ohms and K. Wiesener, *J. Electroanal. Chem., 260* (1989) 63.