Investigations of the negative plate of lead/acid cells 2. Verification with 2 V cells

Michel Saakes, Pieter J. van Duin, Alexander C.P. Ligtvoet and Dick Schmal
TNO Environmental and Energy Research, P.O. Box 6011, 2600 JA Delft (Netherlands)

(Received October 16, 1992; in revised form July 8, 1993; accepted July 12, 1993)

Abstract

Tests in 2 V cells were performed to study the cause of the decrease of capacity and cell voltage. It was found that the capacity of aged cells increased significantly when expanders like Indulin C and Na-1-naphthol-4-sulfonate were added. The cell voltage, lowered by an excess of hydrogen evolution, increased after addition of anisaldehyde. The beneficial effect of both the expanders and inhibitor lasted for several tens of cycles. Addition of anisaldehyde in an aged 2 V submarine cell (8.9 kAh), at a temperature of 30 °C, gave an increase of cell voltage of 145 mV. This increase is almost entirely due to an increase in overvoltage of the hydrogen-evolution reaction at the negative plate. Measurements in 2 V cells confirm the results of short time tests on smooth lead electrodes described in part 1.

Introduction

For a long time the selection of inhibitors and expanders for the negative plate of lead/acid cells has been restricted to tests in 2 V experimental cells. In part 1 [1] of this series we proposed a selection procedure for these types of additives. Inhibitors for the hydrogen-evolution reaction (HER) at the negative plate were studied taking d.c. and a.c. measurements at smooth electrodes. The results showed that anisaldehyde and salicylaldehyde strongly inhibit the HER while Indulin C and Na-1-naphthol-4-sulfonate exhibit good expander properties.

In this part we describe tests of inhibitors and expanders preselected in part 1. Inhibitors are tested after artificially poisoning 2 V 60 Ah cells with copper sulfate. Expanders are tested in cells which have been cycled (charge/discharge) many times. Attention will be paid to the agreement between the work performed at smooth electrodes (part 1) and porous electrodes in 2 V cells (this part).

The influence of the temperature on the inhibitor properties of anisaldehyde was also studied. The reason for this is that in practice the temperature varies over a large range. The temperature dependence of the adsorption of anisaldehyde was also studied at a small electrode of pure copper.

Experimental

Measuring setup

Home-built equipment was used for testing 2 V cells (typical capacity 60 Ah). Control was done with a HP 9816 computer, connected to four parallel cells via a

GPIB measurement and control interface system (DI–AN Microsystems), and 2 V charge/discharge equipment. Each cell was started, cycled and stopped separately. Data were stored on floppy disc. Charging was executed following a CC1, CV, CC2 sequence: first charging at constant current (10 A) until the preset gas voltage, E_g (2.4 V) was reached, followed by constant voltage charging at E_g until the current dropped below a lower limit (0.6 A) and ended with charging at constant current (0.6 A). The latter stage lasted until a constant voltage was reached or was stopped after a certain time. For every tenth cycle the current in the last charging state was 0.3 A in stead of 0.6 A. After charging a pause was taken (1 h) before discharging was done at 11.5 A. Discharging was stopped when the cell voltage reached 1.85 V. After a second pause (1 h) charging was started for the next cycle. The parameters recorded were: cell voltage, charge and discharge current, cell temperature, time and cycle number. Calculated parameters were the charge and discharge capacity (Ah). The temperature was kept at 23.0 ± 0.1 °C. In order to avoid stratification cells were purged with nitrogen gas.

Description of the 2 V test cells

2 V cells were constructed using commercially available pasted CSM (copper stretched metal) negative plates (25 cm × 18 cm × 0.5 cm) and tubular positive plates (25 cm × 18 cm × 1.0 cm). The negative plates were stored in a nitrogen atmosphere before use. The Plexiglas container used to construct the cells was 30 cm × 18 cm × 3 cm. In order for the negative plate to limit the capacity, one negative plate was fixed in between two positive plates. The plates were electrically isolated using standard separator material. The space left in the container (less than 0.5 cm) was filled up with Plexiglas-plate material. After the cell was prepared, it was filled with approximately 1 l of 5.2 M sulfuric acid. The cell was then charged directly after electrical connections have been made to the cell.

Description of the 2 V submarine cell

A 2 V 8.9 kAh submarine cell was used. This cell, type 26 UR 8A, manufactured by VARTA (Germany), was ten years old. During these years, the cell was only charged periodically and was not used in active service. The cell was provided with a separate internal cooling of the plates and a gas purging unit.

This cell was first completely charged at a constant current of 200 A. The parameters recorded during charge were the cell voltage, the negative plate potential versus a Hg/Hg_2SO_4 reference electrode and the electrolyte temperature. During charge, the cell was purged with 60 l/h of nitrogen gas using the acid circulation system. The reference electrode was placed outside the cell and connected by a glass tube, at the bottom fixed with a porous glass filter to prevent bubbles entering the reference electrode. The electrolyte temperature was measured with a Pt-100 thermocouple encapsulated in glass and filled with a conducting paste.

Results

Tests on inhibitors and expanders in a 2 V test cell

In order to test inhibitors, selected in part 1, 2 V cells were artificially poisoned with copper sulfate. In Fig. 1 we show the effect of copper sulfate addition on the discharge capacity of a 2 V cell. The increase of the capacity in the first tens of cycles is due to the formation process of the negative plate.

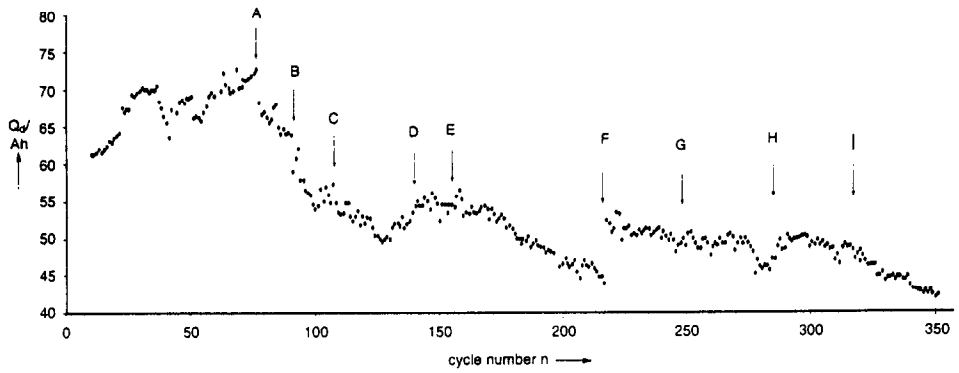

Fig. 1. Effect of copper poisoning and the action of anisaldehyde on the discharge capacity of a 2 V cell; copper sulfate additions at A–C, anisaldehyde additions at D–I.

The addition of copper sulfate is marked by A (0.5 g), B (1.0 g) and C (1.0 g). The discharge capacity shows a strong decrease after copper sulfate addition due to an increased HER at copper sites on the negative plate. Additions of anisaldehyde, selected in part 1, are marked by D (0.22 g), E (0.27 g), F (0.5 g), G (0.5 g), H (1.0 g) and I (0.5 g). The largest improvement of the discharge capacity was found after addition F, which resulted in an increase of 10 Ah on a total capacity of 45 Ah. As can be seen from Fig. 1, the restoring effect of anisaldehyde is maintained for several tens of cycles. The final diminishing of the inhibitor action can be ascribed to the disappearance of anisaldehyde due to oxidation at the positive plate. The question arises why the discharge capacity in Fig. 1, after anisaldehyde has been added for selectively covering copper sites at the negative plate, still shows a steady decrease. A possible explanation for this is the weakening activity of the expander present in the negative plate. To test this hypothesis, we constructed a reference cell, i.e., a cell not artificially poisoned with copper sulfate. In Fig. 2 the discharge capacity is given for this cell.

The increase of the discharge capacity in the first tens of cycles is again due to the formation of the negative porous plate. After this formation, the decrease of the discharge capacity is most probably caused by the diminishing activity of the expander (not by an increase of the HER) which results in an increased size of the lead sulfate crystals and a lowered porosity of the negative lead plate. Experimental evidence for this is found in Fig. 3 where we plotted the charge efficiency, defined as the ratio of the discharge capacity Q_d (at cycle $n-1$) and the charge capacity Q_c (at cycle n). This definition is based on the idea that the charge acceptance depends on the state-of-charge at the last discharge.

The marks given in Fig. 3 (A and B) are the same as in Fig. 2. Figure 3 clearly demonstrates that the decrease of the discharge capacity, shown in Fig. 2, is not caused by the HER since the charge efficiency is almost constant (at $97 \pm 0.5\%$) while the discharge capacity, in the same cycle number range, behaves very differently.

To prove this assumption, we deciced to add an expander (Indulin C [1, 2]), indicated by F and G in Fig. 2. Addition of this expander clearly has a positive influence on the discharge capacity, demonstrating the lowered activity of the expander originally present in the negative plate. The reason why the capacity is not completely restored, is most probably because the process of decrease of porosity is only partly reversible. Therefore, it would be much more effective to maintain a constant level

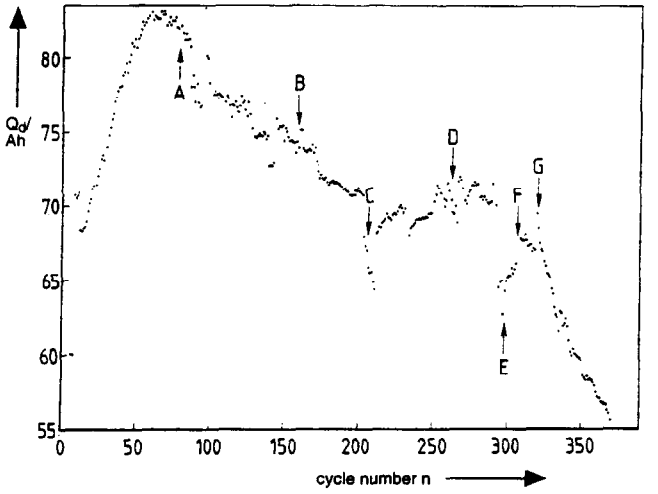

Fig. 2. Effect of anisaldehyde (inhibitor) and Indulin C (expander) on the discharge capacity (Ah) of a 2 V cell; anisaldehyde additions at A–E, Indulin C additions at F and G.

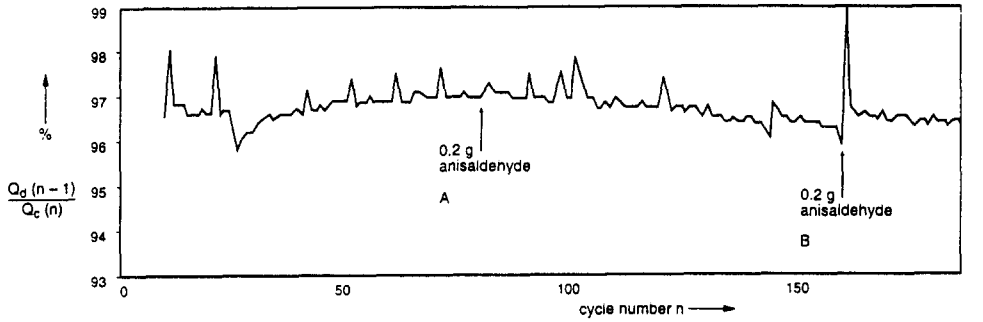

Fig. 3. Charge efficiency of a 2 V test cell. The cycle numbers indicated refer to the cycle number in Fig. 2.

of expander activity (concentration) at the negative plate. This can be accomplished for instance by controlled release of expander by means of a permeable membrane [3].

Besides anisaldehyde, also salicylaldehyde was tested since it was found that this compound also showed good inhibitor properties [1]. In Fig. 4, the charge efficiency is given for a 2 V cell which was artificially poisoned with copper sulfate. Addition of copper sulfate is marked by A (2.0 g) while B and C mark the addition of salicylaldehyde (0.5 g each). The peak at every tenth cycle number, especially visible before the addition of copper sulfate, shows that the charge efficiency is increased due to the equalization charge (0.3 A in stead of 0.6 A). The sharp fall of the discharge capacity, after addition of copper sulfate, is only partly restored after addition of salicylaldehyde during a small number of cycles. We conclude that salicylaldehyde suffers from two shortcomings: (i) the inhibitor action is not strong enough, and (ii) the lifetime is too short to be of any practical importance. Since these shortcomings

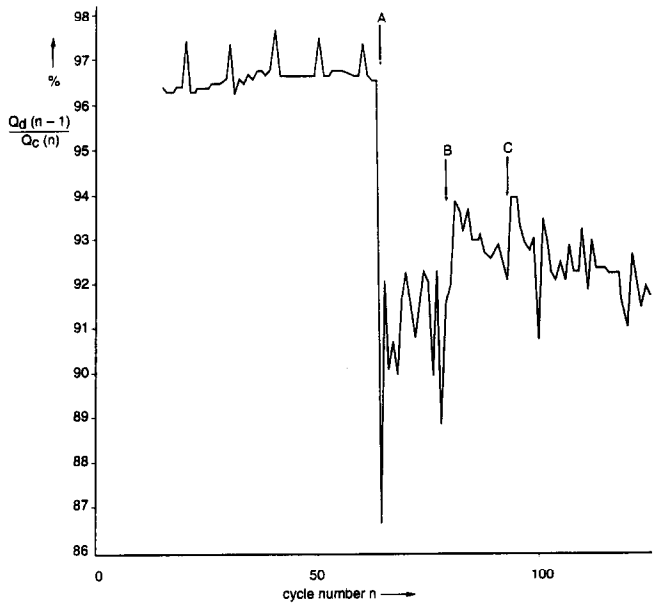

Fig. 4. Effect of copper sulfate and salicylaldehyde on the charge efficiency of a 2 V test cell; copper sulfate addition at A, salicylaldehyde additions at B and C.

apply in much lesser extent to anisaldehyde, we decided to test this inhibitor in a 2 V submarine cell.

From the study in part 1 on the action of Na-1-naphthol-4-sulfonate, known as an expander, we found that an optimum action was present at about 600 ppm. At lower and higher concentrations, the beneficial effect on the capacity was less. To investigate this concentration effect, we cycled a 2 V cell many times (650 cycles) before several additions of Na-1-naphthol-4-sulfonate were made. In Fig. 5, the discharge capacity and the cell voltage of a test cell are given and the effect of the expander mentioned.

The largest increase of capacity is found after an addition of 0.75 g of the expander. The smallest effect is at 0.25 g while at an addition of 2.50 g there is a maximum found in the discharge capacity as a function of time (cycle number). This maximum can be explained by the loss of expander in time, due to the conversion (*e.g.*, oxidation) to less-active material during cycling, which results in the optimum quantity of expander. Estimating the volume of sulfuric acid in the cell is ~1 l and taking the maximum restoring effect equal after addition of 0.75 g, the optimum concentration is around 750 ppm. This value is in good agreement with the earlier a.c. measurements made at the lead/lead sulfate interface [1]. Also the concentration effect measured before is observed in 2 V cells.

The end-of-charge voltage U_{cc2} is found to increase after addition of the expander. This can be explained by the inhibitor action. Another explanation for the increased cell voltage is the higher acid density due to a decreased sulfatation (expander action). The lower value of U_{cc2} every tenth cycle is because of the use of an equalization charge (0.3 A). We conclude that both a.c. impedance measurements [1] and 2 V test cell experiments essentially lead to the same qualitative and quantitative conclusions on the effects of Na-1-naphthol-4-sulfonate on the capacity of the lead/acid cell.

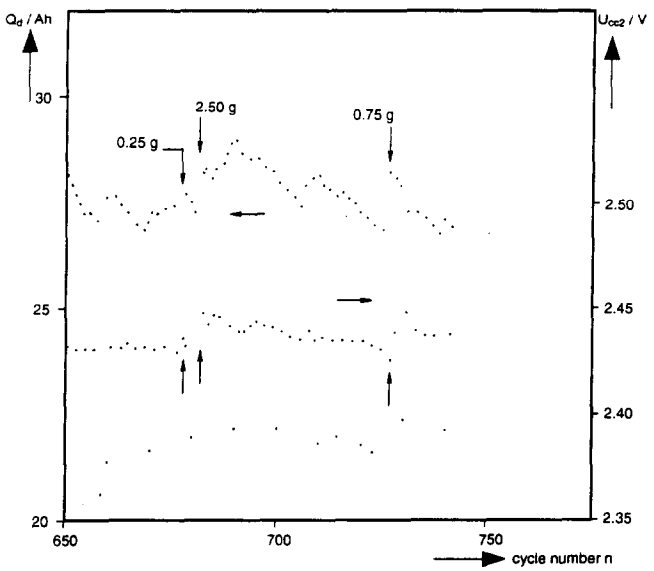

Fig. 5. Discharge capacity and the cell voltage after complete charge of an aged 2 V cell after several additions of Na-1-naphthol-4-sulfonate (expander).

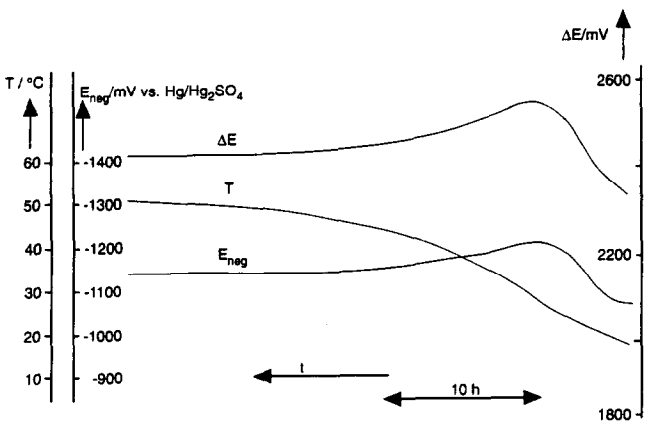

Fig. 6. Change of the cell voltage, negative plate potential and the electrolyte temperature of a 2 V submarine cell at constant current charging at 200 A; 53 g of anisaldehyde has been added.

Tests with anisaldehyde in a 2 V submarine cell

The effect of anisaldehyde was measured in a 2 V submarine cell. Charging with 200 A was continued after addition of 53 g of anisaldehyde. The cell parameters, as measured on *y-t* recorders, are given in Fig. 6 after addition of anisaldehyde. No external cooling of the cell was used.

The temperature in Fig. 6 increases nonlinearly with time. The limit reached (51 °C) in temperature is because the heat exchange with the environment is at equilibrium with the energy input. Somewhat surprising at first glance is the maximum

found for the cell voltage and the negative plate potential as a function of time. To make sure this effect is due to the addition of anisaldehyde, we made two plots of the cell voltage and the negative plate potential as a function of the temperature (Figs. 7 and 8, respectively).

Before discussing Figs. 7 and 8, we will pay attention to the way the cell parameters have been measured. The change of negative plate potential with temperature is complicated by the fact that the reference electrode is at room temperature. In the case where the reference electrode is placed inside the cell, the problem arises that

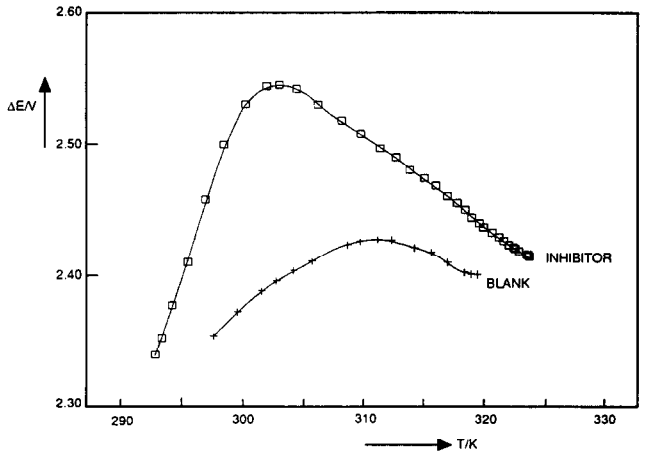

Fig. 7. Change of the cell voltage as a function of temperature for a 2 V submarine cell in the (+) absence (blank) and (□) presence of anisaldehyde (inhibitor); charging was done at a constant current of 200 A.

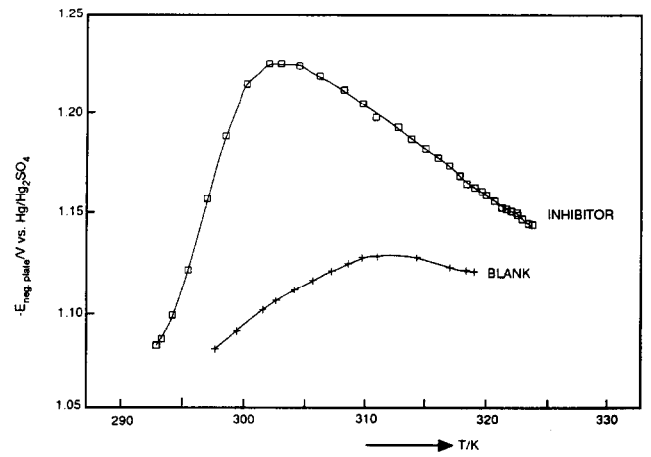

Fig. 8. Change of the negative plate potential of a 2 V submarine cell in the (+) absence (blank) and (□) presence of anisaldehyde (inhibitor); charging was done at a constant current of 200 A.

the reference electrode has no longer a constant potential. Regarding this problem, it would be impossible to study the effect of temperature on the negative plate potential. Fortunately, there is one way out of this situation i.e., by comparing the negative plate both in the absence and presence of an inhibitor. If this is done, and using the same position of the reference electrode, a comparison is allowed.

Comparing Figs. 7 and 8, we first notice that the maximum in cell voltage (Fig. 7, anisaldehyde present) is almost entirely due to the maximum found for the negative plate potential (Fig. 8, anisaldehyde present).

Secondly, from Figs. 7 and 8, we see that if anisaldehyde is absent only a weak maximum is found for the cell voltage and for the negative plate potential. Furthermore, the rise and fall of the cell voltage and the negative plate potential show a linear behaviour. At this stage we only have a qualitative explanation for the maximum present in the cell voltage, which appears to be almost entirely due to the effects of anisaldehyde at the negative plate (inhibitor action): in Fig. 8, however, we first observe a rise in overvoltage for the negative plate. This can be understood as follows. The addition of anisaldehyde in the cell was done by vigorously shaking anisaldehyde with electrolyte solution from the cell. Because of the limited solubility of anisaldehyde an emulsion is formed. We assume that the increase in overvoltage of the negative plate is due to the increased action of the inhibitor at active sites (Cu, Sb). This increased action is because of the enhanced solubility of anisaldehyde at higher temperatures. The maximum in the negative plate potential arises from two opposing effects: decrease in overvoltage (at higher temperature) for the HER and the increase in overvoltage (due to an increase in solubility of anisaldehyde with temperature which results in a higher degree of coverage of active sites). Another explanation of the maximum is that, at higher temperatures, desorption occurs. The maximum effect of anisaldehyde adsorption on the cell voltage, compared with the blank case, is an increase of 145 mV at 30 °C. The temperature used under practical load conditions is about 30 °C which equals the temperature at which a maximum increase is found in Fig. 7.

The quantity of anisaldehyde used in this experiment is not optimized. A much lower quantity may be sufficient.

The general effect of an increasing temperature is a decreasing overvoltage. In the case of anisaldehyde present, we observe an increasing overvoltage from 293 to 303 K. We assume that after addition of the inhibitor the anisaldehyde concentration increases with the rising temperature gradually leading to an increasing surface coverage and a higher overvoltage, thus counteracting strongly the general temperature effect. At about 30 °C, these effects balance and, upon further temperature increase, the general temperature effect predominates. Obviously, at about 50–60 °C the electrode potential tends to coincide with the blank curve, which suggests that in that temperature region the inhibitor is desorbed from the negative plate. A separate experiment on the temperature-dependent absorption of anisaldehyde on a copper electrode confirms this view. Figure 9 shows the Arrhenius plots of a copper electrode in the presence and absence of 200 ppm anisaldehyde. The currents were measured at -0.7 V versus SCE while the reference electrode was kept at room temperature. The electrolyte was 5 M sulfuric acid. Both curves (blank and inhibitor) coincide at approximately 52 °C.

For the submarine cell it was found that after prolonged charging at a constant current of 200 A the negative plate potential was almost equal for the blank case (-1145 mV), and in the presence of anisaldehyde (-1143 mV) at a temperature of 51 °C. The blank curve in Fig. 8 gives a somewhat less negative value for the negative plate potential at 51 °C. The difference however is small (about 20 mV).

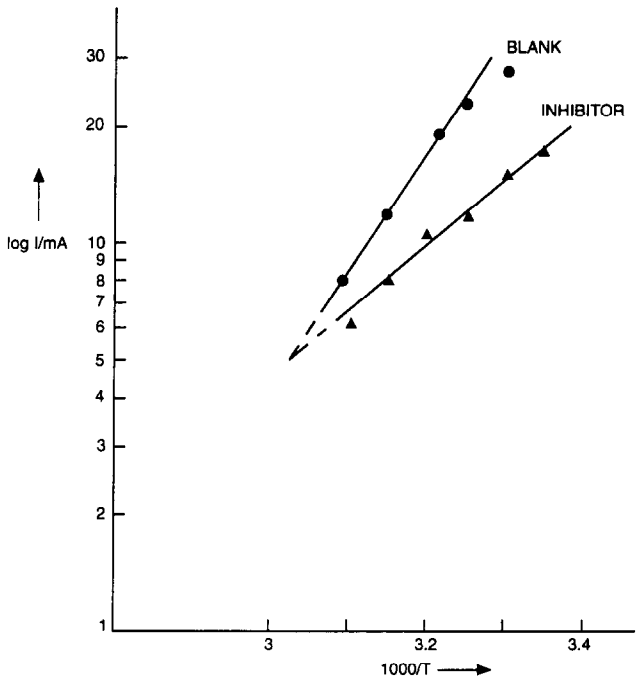

Fig. 9. Plot of log I vs. $1000/T$ for the HER at copper in 5 M sulfuric acid in the (●) absence (blank) and (▲) presence (inhibitor) of 200 ppm anisaldehyde; potential was −0.7 V vs. SCE (at room temperature).

We conclude from the experiment with the submarine cell that the most beneficial effect of anisaldehyde is found at a temperature of approximately 30 °C. The measured effect, an increase of cell voltage of 145 mV at 30 °C, at constant current charging of 200 A, is of practical importance since, at normal conditions, water cooling keeps the temperature at ~30 °C in stead of 51 °C as reached in our experiments (no cooling). Further work is necessary to find the optimum concentration and the lifetime of anisaldehyde in the cell.

Discussion and conclusions

From the work presented, we conclude that the decrease of the capacity of the negative plate of a lead/acid cell has at least two causes: (i) the decrease of expander action, and (ii) the increase of hydrogen evolution. Both aspects have been studied separately. From this study we found that an effective HER inhibitor is anisaldehyde while Indulin C and Na-1-naphthol-4-sulfonate can be used as expander. For the latter expander it was found that the optimum concentration ranges from 600 to 700 ppm at which concentration the largest increase in capacity is found.

An important conclusion is that there exists a good agreement between the results found in 2 V test cells and those obtained earlier [1] using small-scale smooth electrodes.

The effect of temperature on the action of anisaldehyde, studied in a 2 V submarine cell, was found to be most beneficial at ~30 °C. For the submarine cell studied, an increase of 145 mV was found for the cell voltage at a constant current charge of

200 A. Because the operating temperature of these cells is about 30 °C this result is of practical significance.

Acknowledgements

The authors wish to express their gratitude to Messrs. H.E. Wijers, B. van de Ploeg and C. Posthumus of the Royal Netherlands Navy for their stimulating contributions to the project. They further acknowledge the Royal Netherlands Navy, TNO Defence Research and TNO Environmental and Energy Research for their financial support. The work was carried out under contract nr. A81/KM/074.

List of symbols

ΔE	cell voltage, V
E_{neg}	negative plate potential, V
I	d.c. current, A
n	cycle number
Q_c	charge capacity, Ah
Q_d	discharge capacity, Ah
T	temperature, K

References

1 M. Saakes, P.J. van Duin, A.C.P. Ligtvoet and D. Schmal, *J. Power Sources, 46* (1993) 129–147.
2 K.V. Rybalka and M. Etman, *J. Electroanal. Chem., 148* (1983) 73.
3 K. Ledjeff, VARTA Batterie AG, *Ger. Patent No. 0 092 604* (Nov. 30, 1982).