Influence of H_2SO_4 concentration on lead-acid battery performance H-type and P-type batteries

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Abstract

With commercialization of the VRLA battery design the H_2SO_4 concentration of the electrolyte filled in the battery has increased to over 1.30 g cm^{-3}. On the other hand, it has been established that the electrochemical activity of PbO_2 depends on the concentration of H_2SO_4, the highest activity being achieved in solutions with concentrations from 1.10 to 1.28 s.g. H_2SO_4. At $C_{H_2SO_4} > 1.29$ g cm^{-3}, the $PbO_2/PbSO_4$ electrode gets partially passivated. The present investigation determines the initial capacity performance and the changes in battery capacity on cycling of 12 V/32 A h batteries with six different electrolyte concentrations between 1.15 and 1.33 s.g. H_2SO_4. The batteries are cycled with two discharge currents, 3.2 and 8 A. The utilization of PAM is 50% against 37% NAM utilization. The utilization of H_2SO_4 ($\eta_{H_2SO_4}$) varies between 38 and 88%, depending on the concentration of H_2SO_4 in the electrolyte ($C_{H_2SO_4}$). At $C_{H_2SO_4} = 1.24$ g cm^{-3}, $\eta_{H_2SO_4} \approx \eta_{PAM}$. At $C_{H_2SO_4} < 1.24$ s.g., the H_2SO_4 concentration limits the capacity of the battery (H-region of H_2SO_4 concentrations), whereas at $C_{H_2SO_4} > 1.24$ s.g., the capacity of the battery is limited by PAM (P-region). It has been established that in the P-region of H_2SO_4 concentrations, the initial capacity of the battery is higher than the rated value (C_0), but the life of the battery is short (maximum 100 cycles). In the H-region of H_2SO_4 concentrations, the initial capacity is lower than C_0, but the cycle life is considerably longer than 100 cycles and depends on the discharge current and the H_2SO_4 concentration. The voltage of charged cells on open circuit declines with decrease in H_2SO_4 concentration, which allows charging of batteries at lower voltages, as is the case with IT batteries, and reversible sulfation of the plates is avoided as well. The obtained results of the present investigation suggest that lead-acid batteries can be divided in two types depending on the concentration of H_2SO_4 in them: H-type batteries with $C_{H_2SO_4} < 1.24$ s.g., and P-type batteries with $C_{H_2SO_4} > 1.24$ s.g. Currently, VRLA batteries of the P-type are commercially produced. H-type batteries have lower initial capacity than the rated value, but long cycle life and allow to be charged at lower voltages (e.g. 2.27 V per cell). P-type batteries have initial capacity higher than or equal to the rated value, but short cycle life and require high charge voltages.

1. Introduction

The lead dioxide active mass in the lead-acid battery is built of particles and agglomerates interconnected in aggregates and skeleton [1,2]. The PbO_2 particles and agglomerates, in turn, consist of crystal and hydrated (gel) zones [3]. Hydrated zones exchange ions with the H_2SO_4 solution and are in equilibrium with the crystal zones [4]. It is in the hydrated zones that the electrochemical reaction of PbO_2 reduction proceeds during battery discharge [5] and oxygen is evolved as a result of water decomposition during overcharge [6]. Gel zones interact with the H_2SO_4 solution and the latter influences the electrochemical activity of PAM. It has been established that lead dioxide is electrochemically active in the concentration range from 1.10 to 1.28 s.g. H_2SO_4 [7,8]. Within this concentration range, H_2SO_4 dissociates to HSO_4^- and H^+ ions and β-PbO_2 is predominantly formed in PAM.

The aim of the present work is to investigate the correlation between the above influence of H_2SO_4 concentration on the electrochemical activity of the PbO_2 active mass and the capacity and cycle life performance of the lead-acid battery.

Hampson et al. [9] have established that the anodic current flowing through the PAM during oxidation of $PbSO_4$ can be determined by the following equation:

$$i = nFSk \left(C_{Pb^{2+}}^x + C_{H^+}^y \right) \tag{1}$$

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where S is the reaction surface of PbO_2, k is the rate constant, n is the number of electrons involved in the electrochemical reaction. $C_{Pb^{2+}}$ and C_{H^+} are the concentrations of Pb^{2+} and H^+ ions that take part in the anodic reaction, x and y are the reactions orders.

It is evident from Eq. (1) that the rate of $PbSO_4$ oxidation to PbO_2 will depend on the pH of the solution (i.e. on H_2SO_4 concentration). On the other hand, the concentration of Pb^{2+} ions will be determined by the solubility of $PbSO_4$, and the $PbSO_4$ solubility, in its turn, depends on the concentration of the H_2SO_4 solution [10,11]. Thus, the H_2SO_4 concentration influences the charge processes in the lead-acid battery.

Takehara and Kanamura have investigated the influence of H_2SO_4 concentration on the processes of $PbSO_4$ oxidation to PbO_2 [12,13]. They have established that the highest rate of $PbSO_4$ oxidation is in 0.5 M H_2SO_4 solutions (1.048 s.g.). Hattori et al. [14], Mathews et al. [15], Tsubota and co-workers [16] and Eckdunge and Simonsson [17] have found that the concentration of H_2SO_4 affects not only the kinetics of the electrochemical reactions in PAM, but also the utilization of the active materials in the lead-acid battery.

With the introduction of VRLA batteries, the volume of electrolyte in the lead-acid battery was reduced. To compensate for the reduced amount of H_2SO_4 in the cells, its concentration was increased from 1.28 to 1.31–1.34 s.g. H_2SO_4. This technological change was made ignoring the effect of H_2SO_4 concentration on the electrochemical activity of PAM, which might have been the reason for the dramatic decrease in VRLAB cycle life. The above unfavourable situation in the development of the battery industry necessitates ever more in-depth investigations into the influence of H_2SO_4 concentration on the performance of lead-acid batteries. That is, indeed, the aim of the present paper.

2. Experimental set-up

2.1. Battery manufacture

Standard non-formed 3BS SLI positive and negative plates from the current production line of the START battery plant in the town of Dobrich were used. Both positive and negative plates were produced with PbCaSnAl grids. The weight of the positive active mass per plate was 95 g and of the negative active mass was 83 g plate^{-1}.

The plates were formed in H_2SO_4 solution with a density of 1.06 g cm^{-3} employing a formation algorithm developed in our laboratory with initial step-wise increase of the current followed by gradual decrease during the second stage of formation. The formation time was 18 h and the quantity of electricity flowing during the formation process was twice the theoretical capacity of the plates. After formation, the plates were washed and dried at 60 °C for the positive plates and at 140 °C in nitrogen atmosphere for the negative plates, respectively.

The thus produced dry-charged plates were assembled into 12 batteries (12 V/32 A h) comprising three positive and four nega-tive plates per cell. The positive plates were enveloped in AGM separator (H&V, USA) with a thickness of 3 mm (425 g m^{-2}). The compression applied to the active block (comprising positive, negative plates and separators) reduced the seprator thickness by 25%. We chose to use AGM separators despite the flooded battery design so as to avoid expansion of PAM and NAM, which would impair the performance of the batteries. The basic aim of our investigation was to determine the infuence of H_2SO_4 concentration on the electrochemical activity of the positive plates.

The cells were flooded with 530 ml of electrolyte per cell so that a "mirror" was formed over the plates but no free electrolyte volume remained above the active block. Thus, a maximum electrolyte volume was involved in the charge and discharge processes. This electrolyte level was maintained throughout the cycling test. The frequency of water additions is indicated in the respective cycling curves. Six different H_2SO_4 solutions were used with the following concentrations: 1.15, 1.18, 1.21, 1.24, 1.27 and 1.33 g cm^{-3}. Two batteries were filled with each of the above solutions. The above technology of battery manufacture ensured identical initial structure of the positive and negative active masses. During battery cycling, the structure and properties of the active masses would change depending on the H_2SO_4 concentration and the latter would also determine the capacity and cycle life performance of the batteries.

2.2. Battery cycling tests

First, all batteries were subjected to initial cycling at 10 h rate of discharge for 10 cycles to adjust the PAM and NAM structures to the respective H_2SO_4 concentration. The charge was conducted with $I = 12.5$ A up to 15 V and then further charge continued at $U = 15$ V to 110% overcharge. After the charge and discharge cycles, the batteries were left on open circuit for 30 min.

After the above initial cycles, during which the capacity was measured, the batteries were set to cycle life tests employing two different schedules: C_{10}, 10 h discharge rate ($I_{disch} = 3.2$ A) and C_4, 4 h discharge rate ($I_{disch} = 8$ A). Discharge was conducted down to 1.70 V per cell (at C_{10}) and 1.40 V per cell (at C_4). Charging was performed according to the above-described program used for the initial capacity tests. The battery cycling test was conducted at 25 °C and the end-of-life criterion was when the battery failed to deliver 70% of its rated capacity.

2.3. Electrochemical equivalent for H_2SO_4 solutions with regard to concentration

Fig. 1 presents the correlation between the electrochemical equivalent for 1 l of H_2SO_4 solution as a function of H_2SO_4 concentration in g cm^{-3}. The data are taken from Bode's book [18]. The data from this figure will be used for calculating the specific capacity of H_2SO_4 as an active material involved in the reactions that proceed at both types of electrodes.
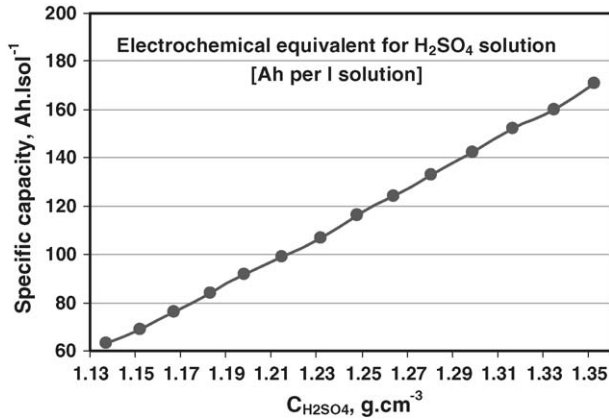
Fig. 1. Electrochemical equivalents for H_2SO_4 depending on its concentration in the lead-acid battery [18, p. 43].

3. Results and discussion

3.1. Correlations between utilization of the active materials (PAM, NAM and H_2SO_4) and H_2SO_4 concentration in the battery

Fig. 2 presents the utilization of the active materials (η_{PAM}, η_{NAM} and $\eta_{H_2SO_4}$) as a function of H_2SO_4 concentration. The calculated utilization coefficient of PAM during discharge is 50% against 37% calculated for NAM. Based on the PAM utilization coefficient, the rated capacity of the batteries was calculated to be 32 A h.

The investigated H_2SO_4 concentration range can be divided in two regions with regard to the utilization of H_2SO_4:

(a) $C_{H_2SO_4} < 1.24\,\mathrm{g\,cm^{-3}}$. In this concentration region the utilization coefficient of H_2SO_4 is the highest (from 52 to 87%). Hence, H_2SO_4 limits the capacity of the cells and thus the cycle life of the batteries. We will call this concentration region H-region and the batteries with the above concentration of H_2SO_4 as H-type batteries.

(b) $C_{H_2SO_4} > 1.24\,\mathrm{g\,cm^{-3}}$. In this concentration region the utilization of PAM is the highest. It is PAM structure and phase
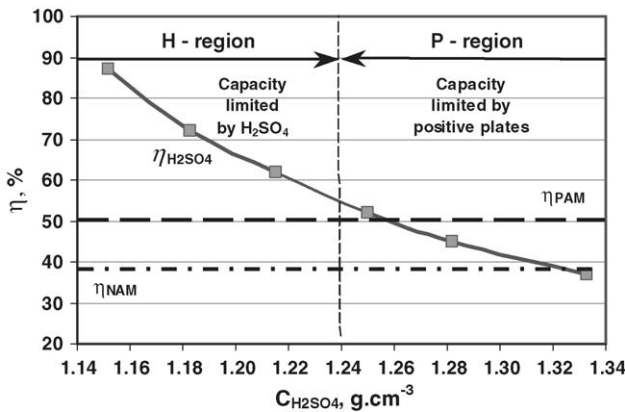

Fig. 2. Utilization of H_2SO_4 as a function of its concentration in the lead-acid battery. The specified utilization of PAM is 50% and the NAM utilization is 37%.
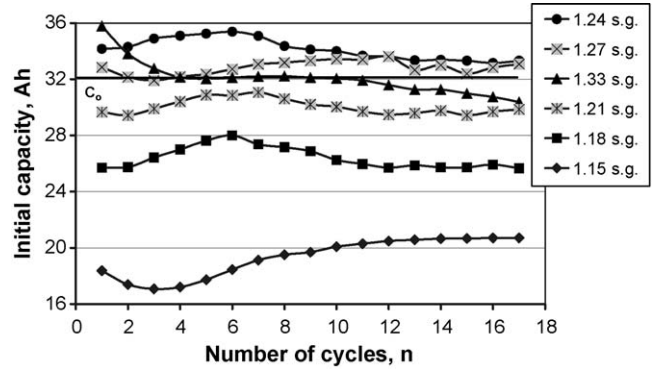

Fig. 3. Initial capacities (on cycling at 10 h discharge rate) for the six types of batteries with different H_2SO_4 concentrations.

composition that limit the capacity and cycle life of the batteries. We will call this concentration region P-region and the batteries with the above H_2SO_4 concentration as P-type batteries. Currently, VRLA batteries of the P-type are commercially available. It has been established that the proportion between gel and crystal zones in the PbO_2 particles and agglomerates changes depending on the H_2SO_4 concentration [8]. At $C_{H_2SO_4} > 1.30\,\mathrm{g\,cm^{-3}}$, the share of gel zones decreases considerably, which results in a substantial decrease in capacity of the $PbO_2/PbSO_4$ electrode. So the original reason for the decline in electrode capacity is actually the H_2SO_4 concentration, which is responsible for the changed proportion between the gel and crystal zones in the particles.

(c) $C_{H_2SO_4}$ around $1.24\,\mathrm{g\,cm^{-3}}$. At this H_2SO_4 concentration, the utilization coefficients of both PAM and H_2SO_4 are almost equal ($\eta_{PAM} = 50\%$, $\eta_{H_2SO_4} = 52\%$).

The present investigation aims to establish the influence of the above two H_2SO_4 concentration regions on the performance of lead-acid batteries.

3.2. Initial capacity of the batteries cycled at 10 h discharge rate

The measured initial capacities versus the number of cycles are presented in Fig. 3. The initial capacity values until the 10th cycle are average values from the tests of the two batteries (later cycled at 10 and 4 h rate of discharge). After the 10th cycle, the results are only for the battery set to 10 h discharge cycling.

During the first cycles, certain changes occur in the structures of PAM and NAM. The active mass structure obtained after the formation process (at $C_{H_2SO_4} = 1.06\,\mathrm{g\,cm^{-3}}$) is transformed into the structure corresponding to the respective H_2SO_4 concentration. Hence, the C_{10}/cycle number curves feature a minimum followed by gradual increase up to a maximum that corresponds to the new active mass structure formed at the respective H_2SO_4 concentration.

P-type batteries exhibit a capacity higher than the rated value of 32 A h during the first cycles, after which their capacity declines. H-type batteries have a capacity lower than the rated
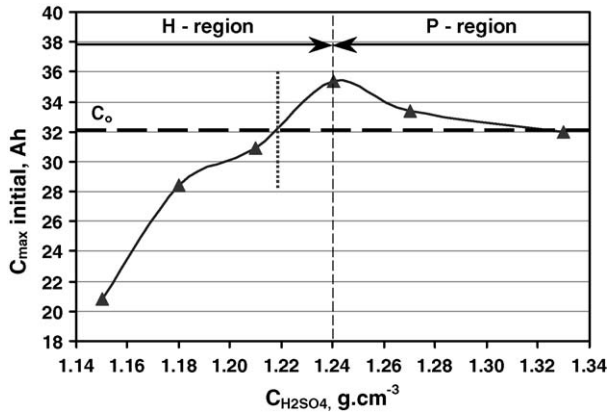
Fig. 4. Maximum initial capacity (on 10 h discharge cycling) for the six types of batteries with different H_2SO_4 concentrations.

value (C_0). The battery with $C_{H_2SO_4} = 1.21 \, \text{g cm}^{-3}$ has capacity performance closest to C_0. Its maximum initial capacity is $C_{max} = 30.9 \, \text{A h}$, which is by 3.4% lower than the rated value.

3.3. Determination of the H_2SO_4 concentration yielding maximum initial capacity equal to the rated value

Fig. 4 presents the measured maximum initial capacity values C_{max} as a function of H_2SO_4 concentration. It can be seen from the data in the figure that $C_{max} = C_0$ at $C_{H_2SO_4} = 1.22$ and $1.33 \, \text{g cm}^{-3}$.

Fig. 5 gives the C_{max} values as a function of H_2SO_4 utilization. The data in the figure indicate that the battery meets the requirement to reach maximum initial capacity within the first 10 cycles when the utilization of H_2SO_4 is $\eta_{H_2SO_4} \leq 57\%$. This corresponds to $C_{H_2SO_4} = 1.22 \, \text{g cm}^{-3}$.

3.4. Charge and discharge U/t curves for the batteries with different electrolyte concentrations

The electromotive force (E) for the lead-acid cell depends on the concentration of H_2SO_4 according to the equation:

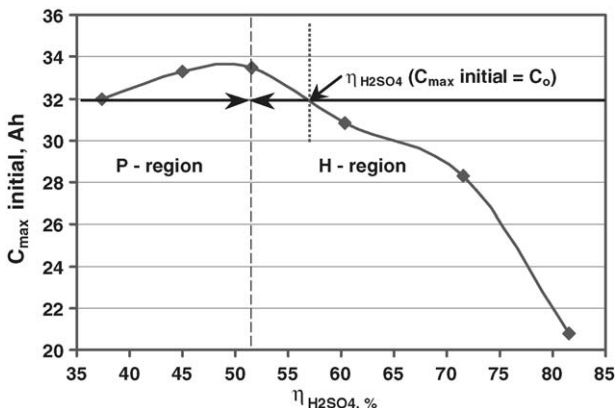$$E = E_0 + \left(\frac{RT}{F} \right) \ln \left(\frac{a_{H_2SO_4}}{a_{H_2O}} \right) \qquad (2)$$

Fig. 5. Maximum initial capacity (on 10 h discharge cycling) as a function of H_2SO_4 utilization.
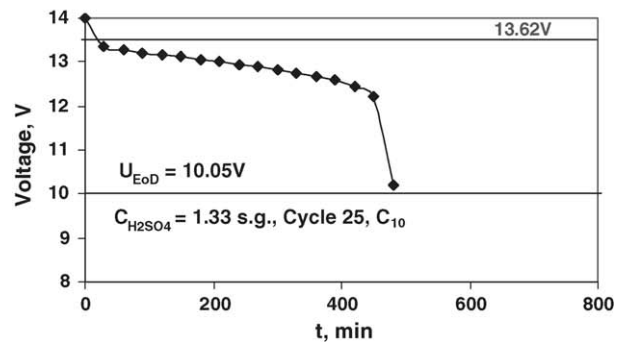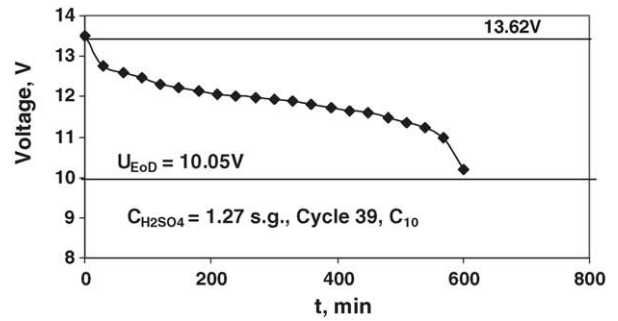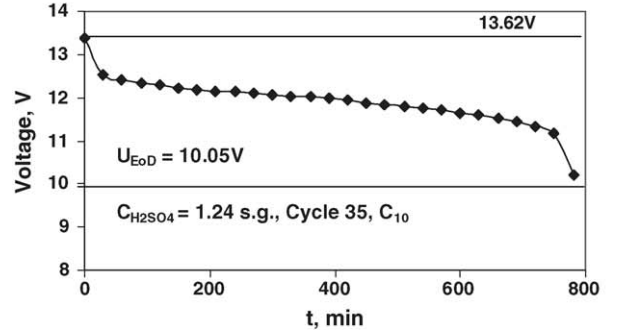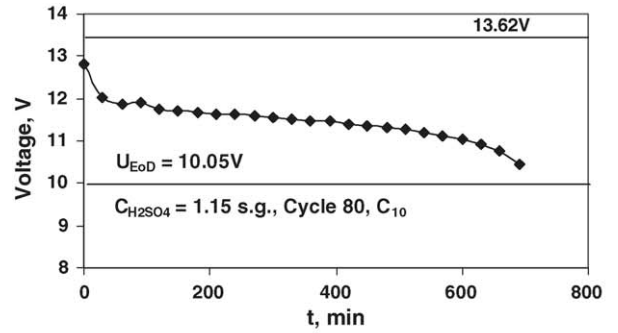

Fig. 6. Changes in battery voltage on discharge with a current of 3.2 A.

At 25 °C, $E_0 = 2.040 \, \text{V}$. As the H_2SO_4 concentration is high, a_{H_2O} is not constant and cannot be included in E_0. The cell voltage depends on the concentration of H_2SO_4 and this dependence should be taken into account during battery charge.

Batteries with different electrolyte concentrations were set to cycling at two discharge currents corresponding to 10 and 4 h rate of discharge. The discharge curves, obtained during the first half of battery life, for batteries with four H_2SO_4 concentrations are presented in Fig. 6. The first value (at $t = 0$) gives the battery voltage on open circuit 30 min after charge. For comparison,
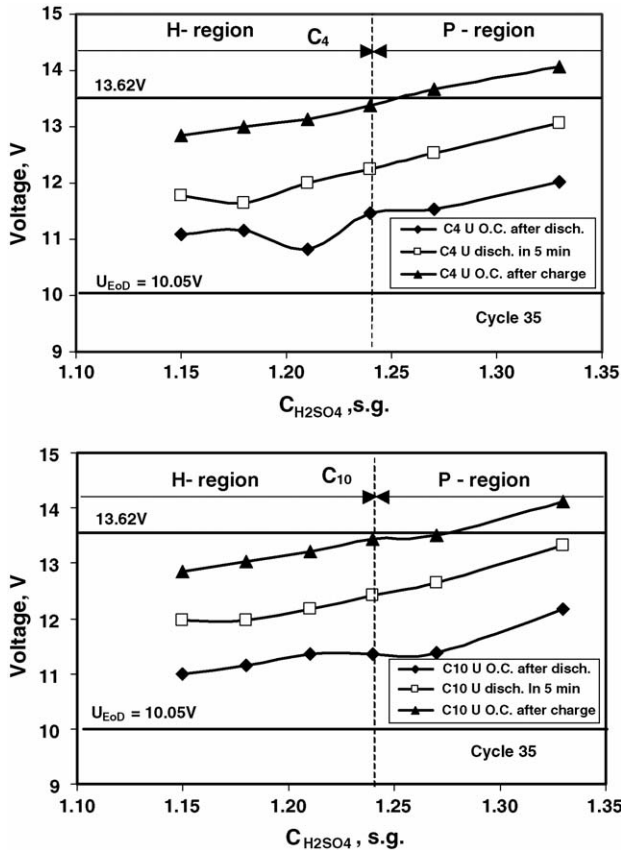
Fig. 7. Battery voltage (measured after 30 min open circuit stay following charge) (▲); after discharge (♦); 5 min after the beginning of discharge (□) as a function of H_2SO_4 concentration.

Fig. 8. Battery voltage vs. time of charge with 12.5 A up to 15 V. The preceding discharge was conducted with 3.2 A.

the figure gives also the charge voltage (13.62 V per battery or 2.27 V per cell) and the end-of-discharge voltage (10.05 V) required for batteries for IT systems. We have not used this charge voltage in our experiments.

The data in Fig. 6 evidence that with increase of the H_2SO_4 concentration, the battery voltage on open circuit increases, too. At constant charge voltage (e.g. 13.62 V), the batteries with $C_{H_2SO_4} = 1.27\,\mathrm{g\,cm^{-3}}$ will charge slowly, whereas those with $C_{H_2SO_4} = 1.33\,\mathrm{g\,cm^{-3}}$ will be charged only partially. That is why it is very important that the electrolyte concentration in the lead-acid battery is selected accounting for the voltage capabilities of the charging device. When the supplied charging voltage is low (13.6–13.8 V), the battery should be of the H-type, i.e. H_2SO_4 concentration in the electrolyte below $1.24\,\mathrm{g\,cm^{-3}}$.

Fig. 7 shows the measured voltages for batteries with different H_2SO_4 concentrations after discharge (after 30 min stay on open circuit) (♦), 5 min after the beginning of discharge (□), and after charge (after 30 min stay on open circuit) (▲). The charge voltage (13.62 V) and the end-of-discharge voltage (10.05 V) are also given in the figure.

The data in Fig. 7 evidence that at H_2SO_4 concentrations higher than $1.30\,\mathrm{g\,cm^{-3}}$, the battery does not charge fully at 13.62 V. Hence, if the above charge voltage is used, the batteries should be of the H-type to avoid reversible sulfation.

Fig. 8 presents the charge curves (for 150 min) of batteries with different H_2SO_4 concentrations after 10 h discharge, and
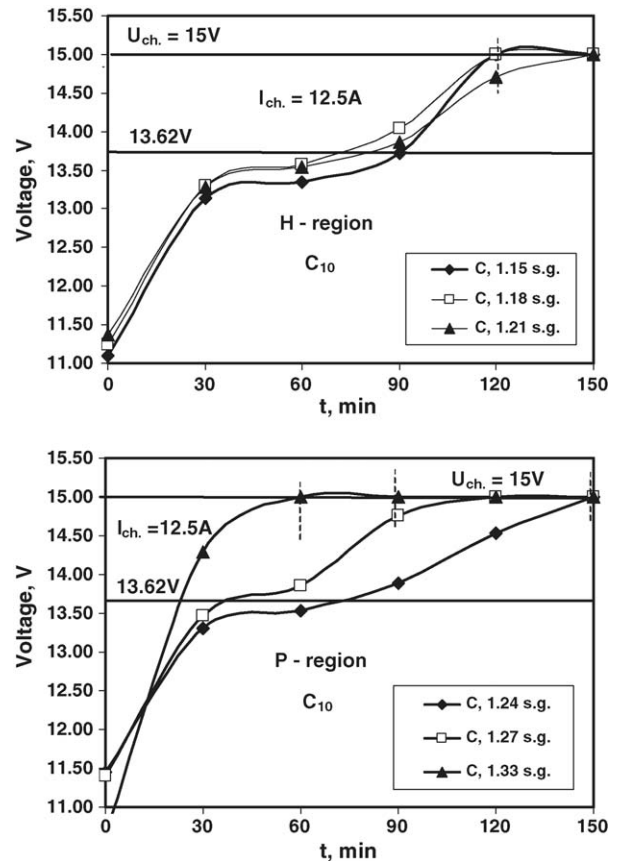
Fig. 9 shows similar curves for batteries cycled at 4 h discharge rate.

It is well known that the charge process of both PAM and NAM proceeds in two stages: during the first stage $PbSO_4$ is oxidized to PbO_2 in PAM and it is reduced to Pb in NAM. When the battery reaches about 70% state of charge, the electrochemical reaction of charge at the positive plates is no more able to maintain the current constant and the potential of the positive plates begins to increase tending to involve another electrochemical reaction in the current consumption process. Such an electrochemical reaction is the decomposition of water (second stage of charge). The later the latter process starts, the higher the charge acceptance of the battery and thus the better the efficiency of the charge process.

The data in Figs. 8 and 9 give grounds for the following conclusions:

(a) The profile of the charge curves depends on the current and capacity of the preceding discharge.
(b) The charge curves, and especially the efficiency of the charge process, depend on the concentration of H_2SO_4. The value of 15 V is achieved the fastest, i.e. the charge process is least efficient, at H_2SO_4 concentration of $1.33\,\mathrm{g\,cm^{-3}}$. Charging of batteries is most efficient, irrespective of the discharge rate, when the concentration of H_2SO_4 in the electrolyte is lower than $1.24\,\mathrm{g\,cm^{-3}}$. On C_4 discharge (Fig. 9)
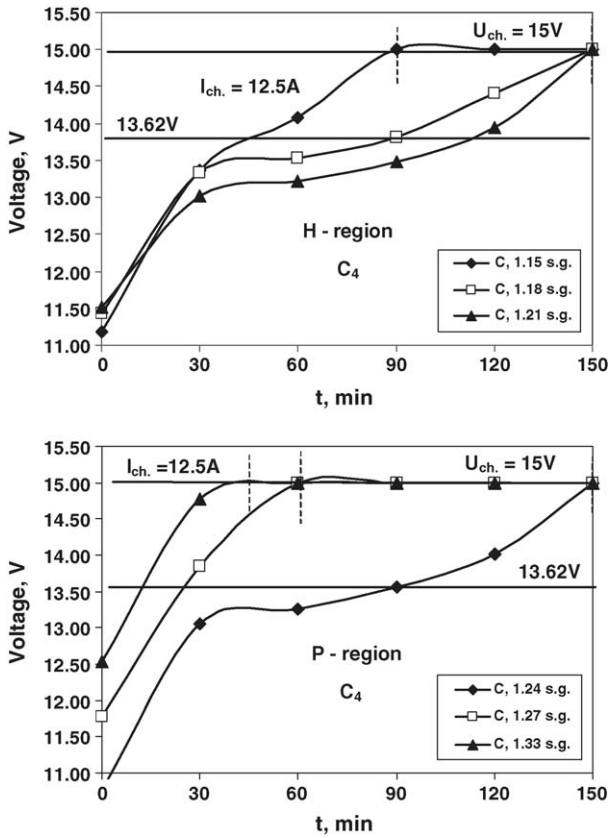
Fig. 9. Battery voltage vs. time of charge with 12.5 A up to 15 V. The preceding discharge was conducted with 8 A.

and $C_{H_2SO_4} = 1.15\,g\,cm^{-3}$, the battery reaches 72% state of charge (SOC) for 1 h and after 90 min its SOC is 88%.

It follows from all above said that H-type lead-acid batteries are more readily charged than P-type batteries. A possible explanation of this finding could be looked for in the correlation between PbSO$_4$ solubility and H$_2$SO$_4$ concentration, which is presented in Fig. 10 [10,11]. The solubility of PbSO$_4$ is much higher in the H-region of H$_2$SO$_4$ concentrations than in the P-region. Hence, the PbSO$_4$ crystals will maintain higher con-
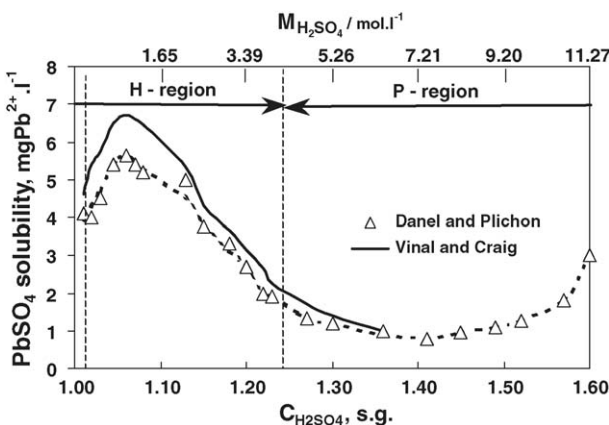

Fig. 10. Dependence of the solubility of PbSO$_4$ crystals on H$_2$SO$_4$ concentration, as determined by Vinal and Craig [10], and Danel and Plichon [11].
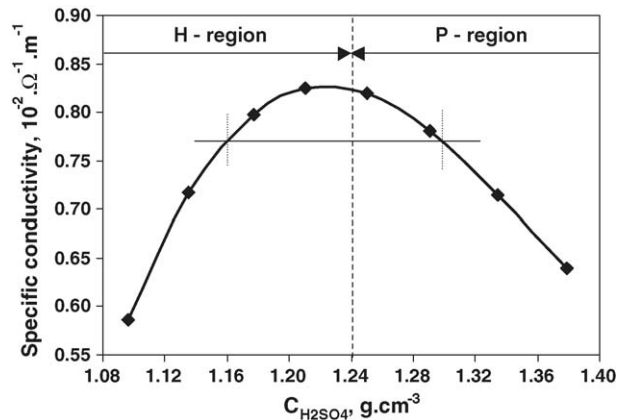

Fig. 11. Dependence of the specific electroconductivity of H$_2$SO$_4$ solution as a function of H$_2$SO$_4$ density [18, p. 75].

centration of Pb^{2+} ions in the solution when the concentration is within the H-region, which will facilitate the charge process (see Eq. (1)). During battery discharge, the H$_2$SO$_4$ concentration decreases. If the H$_2$SO$_4$ concentration in the batteries decreases to 1.10–1.11 g cm^{-3} at the end of discharge, this corresponds to the region of maximum solubility of PbSO$_4$ (see Fig. 10). Hence, these batteries exhibit the highest charge efficiency. Such batteries can be H-type batteries with electrolyte concentrations 1.21 and 1.24 g cm^{-3}.

The power output of lead-acid batteries depends strongly on the conductivity of H$_2$SO$_4$. Fig. 11 presents the specific electroconductivity of H$_2$SO$_4$ solution as a function of its density [18, p. 75]. It can be seen from the figure that within the concentration range from 1.16 to 1.29 s.g. the conductivity is the highest ($\chi > 0.765 \times 10^{-2}\,\Omega^{-1}\,m^{-1}$). An interesting finding is that the maximum electrical conductivity is measured for H$_2$SO$_4$ solution with a density of 1.22 g cm^{-3}, i.e. within the H-region. It can be expected then that the electrolyte in H-type batteries will have sufficiently high electrical conductivity to maintain high power output.

3.5. Cycle life of P- and H-type batteries as a function of H$_2$SO$_4$ concentration

Fig. 12 presents the relationship between battery capacity and cycle number for batteries with different H$_2$SO$_4$ concentrations cycled with discharge current of 3.2 A (10 h discharge rate) and 8 A (4 h discharge rate) down to end-of-discharge voltage of 1.70 V per cell (C_{10}) and 1.4 V per cell (C_4), respectively. The discharge was conducted down to 100% DOD. The end-of-life criterion was accepted to be when the battery capacity fell down to 22 A h, irrespective of the H$_2$SO$_4$ concentration. The cycles during which water was added to the batteries (15–20 ml H$_2$O per cell) are marked in Fig. 12.

The data in Fig. 12 evidence that the capacity of P-type batteries on cycling declines down to a certain value and is arrested at that level for a certain number of cycles after which the capacity decreases until battery end of life. The H-type batteries exhibit an initial capacity decline, passing through a minimum, followed by gradual increase in capacity, which then passes through a flat

maximum (on cycling with C_4 A). The duration of this maximum depends on the concentration of H_2SO_4 in the battery. The more diluted the H_2SO_4 solution (H-type), the longer the cycle life of the battery.

Fig. 13 shows the cycle life of the batteries under test versus H_2SO_4 concentration.

A comparison between the data in Figs. 12 and 13 suggests the following conclusions:

(a) The number of cycles versus $C_{H_2SO_4}$ curves for batteries with 1.24 g cm^{-3} H_2SO_4 concentration pass through a minimum for both discharge cycling modes, i.e. these batteries have the shortest cycle life (Fig. 13).

(b) The cycle life of P-type batteries is short (less than 100 cycles, Fig. 13), but their capacity is high, above the rated
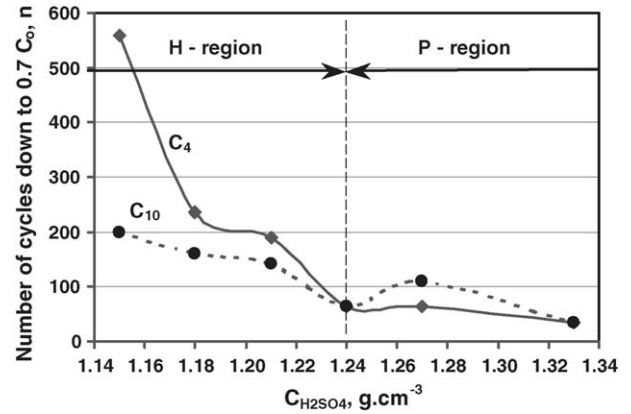

Fig. 13. Cycle life of the batteries under test as a function of H_2SO_4 concentration on cycling with discharge currents, 8 and 3.2 A.
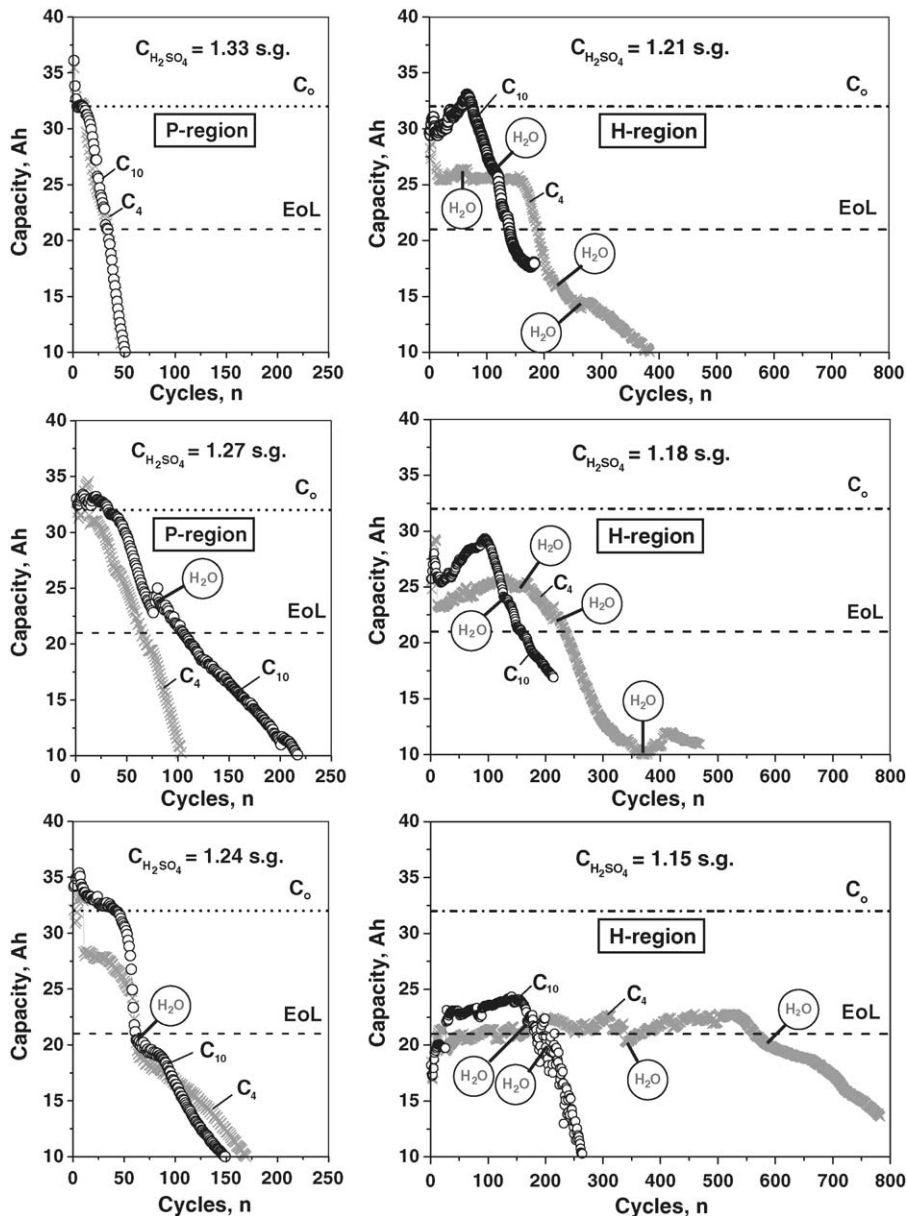

Fig. 12. Capacity vs. number of cycles dependences for batteries with different H_2SO_4 concentrations on cycling with different discharge currents: 3.2 A to 1.70 V, and 8 A to 1.40 V.

value (Figs. 3–5). Obviously, within this H_2SO_4 concentration region the positive plates undergo fast passivation [8] and lose their electrochemical activity, thus reaching early end of life. If the batteries are re-activated, they can endure some more cycles.

(c) Batteries with H_2SO_4 concentrations within the H-region have long cycle life, which increases with decrease in H_2SO_4 concentration (Fig. 13). However, the capacity of these batteries is lower than the rated value and it declines with decrease in $C_{H_2SO_4}$. Moreover, the higher the discharge rate on cycling, the longer the cycle life of these batteries. Thus, on C_4 discharge the battery endures 550 cycles against 200 cycles at C_{10} discharge rate. If we compare these data with the 100 cycles achieved by P-type batteries, we can conclude that the processes that take place in H-type batteries differ essentially from those in P-type batteries. That is the reason for the more than twice longer cycle life of H-type batteries as compared to their P-type counterparts.

The observed differences in behaviour of P- and H-type batteries on cycling indicate that there is a difference between the processes that occur in the two H_2SO_4 concentration regions. These experimental findings give us grounds to distinguish two types of lead-acid batteries with regard to the H_2SO_4 concentration of the electrolyte they are filled with, namely P-type and H-type lead-acid batteries.

4. Conclusions

The performance of 12 V/32 A h batteries with different H_2SO_4 concentrations (between 1.15 and 1.33 g cm^{-3}) has been investigated at 50% PAM utilization and 37% NAM utilization. Two H_2SO_4 concentration regions have been distinguished: $C_{H_2SO_4} < 1.24$ g cm^{-3} (H-region) in which H_2SO_4 limits the capacity of the battery (H-type batteries), and $C_{H_2SO_4} > 1.24$ g cm^{-3} (P-region) in which the lead dioxide plates limit the capacity of the battery (P-type batteries). Batteries with H_2SO_4 concentration above 1.22 g cm^{-3} have a capacity higher than or equal to the rated value during the first 10 cycles. This latter concentration corresponds to 57% utilization of H_2SO_4. Below this concentration, the battery cannot reach its rated capacity within the first 10 cycles.

The concentration of H_2SO_4 should be chosen taking into account the standard charge voltage employed by the battery user. When the specified charge voltage is lower than 14 V, the batteries should be filled with electrolyte with H_2SO_4 concentration within the H-region so as to allow complete charge of the batteries and to avoid reversible sulfation. H-type batteries ($C_{H_2SO_4} < 1.24$ g cm^{-3}) operate within the concentration region of enhanced solubility of $PbSO_4$ and hence improved charge efficiency. On cycling at 4 and 10 h discharge rate (100% DOD), P-type batteries have shorter cycle life (max. 100 cycles), whereas H-type batteries have long cycle life (200–250 cycles),

depending on $C_{H_2SO_4}$ and on the discharge current. These experimental results give us grounds to divide lead-acid batteries in two types:

P-type batteries, $\quad \eta_{PAM} = 50\%, \quad \eta_{H_2SO_4} < 57\%,$ $\eta_{NAM} \leq 40\%$

H-type batteries, $\quad \eta_{PAM} = 50\%, \quad \eta_{H_2SO_4} > 57\%,$ $\eta_{NAM} \leq 40\%$

P-type batteries are currently produced as commercial VRLABs and have higher initial capacity, but shorter cycle life. The experimental data reported in this paper evidence that H-type batteries have a bit lower initial capacity, but considerably longer cycle life than their P-type counterparts.

The boundary $\eta_{H_2SO_4}$ value between the two types of batteries depends on battery design and grid alloy used. Sb and PbSb alloys have been found to increase the share of hydrated (gel) zones in the PbO_2 particles and agglomerates [19]. This will influence the ion exchange between the solution and the hydrated PbO_2 zones, which, in turn, affects the activity of the PbO_2 plate and hence the boundary $\eta_{H_2SO_4}$ value between the two types of batteries.

The observed influence of H_2SO_4 concentration on the behaviour of lead-acid batteries and the clear distinction between the two types of LAB imply that, most probably, it is the high H_2SO_4 concentration in VRLAB that limits the cycle life performance of these batteries. Maybe, the performance of VRLAB could be improved substantially if H_2SO_4 solutions with concentrations within the H-region are employed, moreover that, as a rule, these batteries are charged with lower voltages.

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