STUDY OF STRUCTURAL FACTORS OF LEAD–ACID BATTERY ELECTRODES

K. MICKA and M. SVATÁ

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Prague 10 (Czechoslovakia)

V. KOUDELKA

Pražská akumulátorka, n.p., 293 01 Mladá Boleslav (Czechoslovakia)

Summary

The electrolyte conductivity in the pores, and the true and apparent densities of the active mass, were measured on electrodes of a starter-type lead–acid battery in various stages of discharge, and the porosity of the plates and the tortuosity factor of the pores were evaluated. The results suggest that the charged, cycled positive plates contain a certain fraction of lead dioxide of a lower density, probably amorphous, which is reduced preferentially. Transport restrictions are more important in positive than in negative plates. Volume changes of a negative plate during cycling were found to be reversible, while with a positive plate they were irreversible.

Introduction

Data in the literature on the porosity and tortuosity factor of battery electrodes are scarce, although they are needed both in the theory of such electrodes and in checking their quality. We have introduced a method of measurement of these characteristics, which is relatively simple and accurate, and we have applied it to Ni–Cd battery electrodes [1]. As a continuation of this work, the present paper deals with the positive and negative plates for starter-type lead–acid batteries with the object of obtaining some information about structural changes taking place during their discharge.

Experimental

The true (without pores) densities of the active mass were measured pycnometrically in toluene, the apparent (including pores) densities in a vacuum mercury densitometer at 900 mmHg. The negative active mass was protected with a film of stearic acid to prevent amalgamation. The method

of measurement of the electrolyte conductivity in the pores has been described earlier [1]. The charge–discharge cycles and other measurements were made on commercial electrodes of dimensions 14.3 × 13.4 cm and thickness 0.20 cm (positive plates) or 0.18 cm (negative plates). They contained 126 ± 1 g of positive and 91 ± 1 g of negative active mass in the formed dry state (the practical tolerance limits are indicated). The electrodes were assembled in cells between two counter-electrodes of opposite polarity and with an excess of electrolyte (sulphuric acid of a density of 1.28 g/cm^3 or 4.9M) so that the cell capacity was limited by the capacity of the tested electrode. The positive electrodes were subjected to ten, the negative ones to two, cycles at a ten-hour discharge rate (I = 3.2 mA/cm^2) to an end cell voltage of 1.70 V.

After the electrodes had developed their full capacity, they were analysed in the charged state and their capacity was determined as a function of the discharge current density to an end voltage of 1.0 V per cell. Their porosity was determined by two independent methods. (a) After discharging, the electrodes were left in the electrolyte for about two hours to equilibrate the concentrations in the pores and in the bulk and were then withdrawn. The adhering electrolyte was allowed to drop off for one minute, and the pore electrolyte was leached out into water in four successive steps of 15 min each. All the extracts were combined and the content of H_2SO_4 determined titrimetrically. From this, the pore volume of the plate was calculated, which, on dividing by the volume of the active mass (i.e., the volume of the plate minus the volume of the grid) gave the porosity. This will be referred to as the titrimetric porosity. The results were reproducible to within ± 0.01. (b) From the true and apparent densities, ρ_t and ρ_a, of the dried active mass the porosity was calculated as $V_p = 1 - \rho_a/\rho_t$. This will be referred to as the pycnometric porosity.

The content of lead sulphate in the active mass was determined by dissolving the other components in nitric acid, dissolving the residue in an ammonium acetate solution and titrating complexometrically. Lead(II) oxide was separated from the active mass by dissolving in dilute acetic acid and titrating complexometrically. Lead dioxide was allowed to react with a solution of potassium iodide in an acetate buffer and the iodine thus formed was titrated with thiosulphate.

Results and discussion

Positive plates

The measured discharge times at current densities of 0.05, 0.1, 0.2, and 0.3 A/cm^2 were 26.1, 10.4, 4.08, and 1.74 min (averages of 4 measurements), in good agreement with the respective theoretical values [2] of 31.2, 10.8, 3.65, and 1.93 min. The experimental errors increased with the current density from ± 1.8 to ± 19% as the knee of the discharge curve became gradually less distinct.

A relation exists between the charge passed during discharge and the true density of the active mass, ρ_t. We denote the percentage contents of PbO_2 and $PbSO_4$ at a charge passed, q, as p_q and p'_q, respectively. The difference, $100 - p_q - p'_q$, can be assigned to lead(II) oxide, which has about the same density as PbO_2 (tetragonal PbO, present in the positive plates [3], has a density of 9.53 g/cm³; rhombic PbO, 8.0 g/cm³; β-PbO_2, 9.37 g/cm³ [4]; α-PbO_2, 9.47 - 9.87 g/cm³ [5, 6]). The α-PbO_2 content is much smaller in cycled plates [5] than is that of the β modification (about 1:4), and the content of PbO was determined as 1.3 - 2.3%, so the densities of these minor components need not be known exactly. From simple considerations it follows that

$$100/\rho_t = p'_q/\rho_1 + (100 - p'_q)/\rho_2. \tag{1}$$

The density of lead sulphate, ρ_1, is 6.20 g/cm³ [4]. If $p'_q = 0$, then $\rho_t = \rho_2 =$ density of the oxides. Now p'_q depends on the charge passed, q (in C/cm²), in the following manner:

$$p'_q = \frac{m_o p'_o + 100 M_1 q/F}{m_o + (M_1 - M_2)q/F}, \tag{2}$$

where M_1 and M_2 denote the molar masses of $PbSO_4$ and PbO_2, respectively, $p'_o = 3.1\%$ (the initial content of $PbSO_4$ in the charged state ($q = 0$)), and m_o is the quantity of the active mass in g/cm² of the charged plate. From the quantity of the formed, dry, active mass, 126 g, and the plate surface area of 192 cm², we obtain $m_o = 0.656$ g/cm².

Thus, the dependence of ρ_t on q can be calculated from the above equations. However, if we use the tabulated density of β-PbO_2 (9.37 g/cm³), then the true density of the charged plate is calculated as 9.22 g/cm³, whereas the measured mean value (from 4 samples) is 8.65 g/cm³. Conversely, if we introduce the latter value in eqn. (1) and calculate the density of the oxide, we obtain $\rho_2 = 8.76$ g/cm³.

Hence, it is apparent that the true density of the oxide in charged positive plates is lower than the tabulated value, and this discrepancy cannot be attributed to the possible presence of oxides other than β-PbO_2 (the content of PbO was found to be negligible), if the known crystalline forms only are considered. The calculated dependence of ρ_t on C, together with the experimental points, is shown in Fig. 1, where C is the total charge per plate and the density of the oxide, ρ_2, was set, in turn, equal to 8.76 and 9.37 g/cm³. The former value provides good agreement with experiment in the range $C = 0 - 4$ A h, and the latter in the range 5 - 20 A h. Reinhardt and coworkers [7] observed that during discharge of a positive plate containing β-PbO_2 the X-ray diagram did not change during the initial discharge period (about 25% of the total discharge time), and the content of β-PbO_2 found by chemical analysis at the beginning of discharge was higher than that found roentgenographically. Hence, they concluded that amorphous PbO_2 was present in their plates at the beginning of the discharge. Their observa-
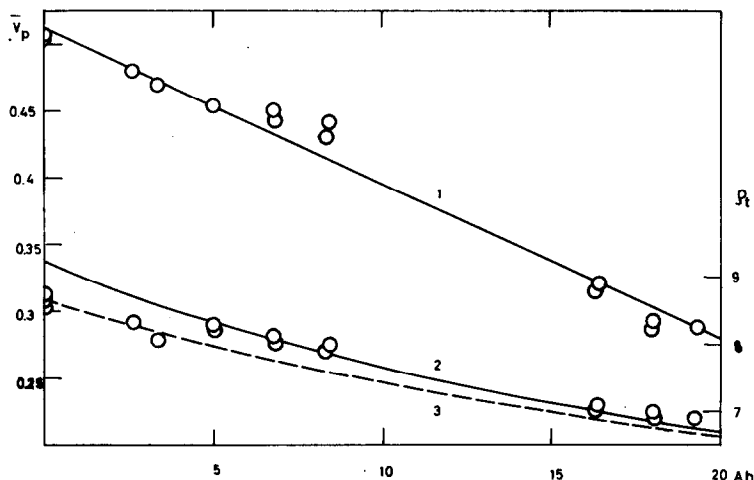
Fig. 1. Dependence of the mean porosity, $\bar{V}_p$ (1), and true density, ρ_t (2, 3), of positive plates on the charge passed. Straight line 1 corresponds to eqn. (5), curves 2 and 3 were calculated from eqns. (1) and (2) with $\rho_2 = 9.37$ and 8.76 g/cm^3, respectively.

tions and ours are in agreement. Amorphous forms of solids are known to have a significantly lower density than the corresponding crystalline modifications. Accordingly, it is probable that the charged plates contain a certain fraction of amorphous PbO_2 of a lower density, which is reduced in preference to the crystalline β-PbO_2 during discharge. Caulder and Simon [8] also consider the amorphous PbO_2 to be the more active form.

The dependence of the porosity, $\bar{V}_p$ (averaged over the plate thickness), on the charge passed is given by the following elementary relationship:

$$\bar{V}_p = V_{po} - (V_{red} - V_{ox})q/2d'F, \tag{3}$$

where $V_{red} = M_1/\rho_1$ and $V_{ox} = M_2/\rho_2$ denote the molar volumes of the reduced ($PbSO_4$) and oxidised (PbO_2) forms, respectively, and $2d'$ is the thickness of the plate corrected for the grid (assumed thickness of the plate in the absence of the grid). From the grid mass per cm^2, 0.343 g, and the density, 10.78 g/cm^3, we obtain the correction for the grid as $0.343/10.78 = 0.032$ cm, which must be subtracted from the plate thickness, $2d = 0.2$ cm, to give $2d' = 0.168$ cm (this is essentially a volume correction). If q is expressed in A h, then eqn. (3) takes the form

$$\bar{V}_p = V_{po} - 0.012\,5C, \tag{4}$$

where $C = 0.106\,7q$ (A h) is again the total charge per plate. (Here we used the earlier mentioned "effective" value of $\rho_2 = 8.76$ g/cm^3 rather than the tabulated one.)

In Fig. 1 the experimental (pycnometric) porosity, V_p, in the range $C = 0 - 20$ A h is shown. The points are fitted by a regression line of the algebraic form (correlation coefficient $r = -0.991$)

$$V_p = 0.512 - 0.011\,6C, \tag{5}$$

whose slope is somewhat smaller than the theoretical. The measured initial porosity (average from four plates) is 0.503.

The fact that the measured decrease in porosity is smaller than that calculated could be attributed to an expansion of the plates during discharge. If we assume that only the volume of the pores increases during this expansion, then $2d'(1 - V_p) = 2d''(1 - V_{p\,exp})$, where d'' and $V_{p\,exp}$ refer to the expanded plate. On calculating $V_{p\,exp}$ from eqn. (5) and V_p from eqn. (4) ($V_{p\,o} = 0.512$), the ratio of d''/d' becomes 1.015 for $C = 10$ A h and 1.025 for $C = 20$ A h. We obtained $d''/d' = 1.01$ from a series of measurements after complete discharge; errors due to non-ideality of the plate surface were eliminated by taking average values from six measurements, which were, however, somewhat affected by the moderate pressure exerted by the micrometer screw. The expansion was not quite reversible ($2d = 0.243$ cm after the second cycle, 0.254 cm after the tenth cycle).

Expansion of positive plates in the charged state during service life was proved indirectly by Dittmann and Sams [9] who measured the apparent density of the plates. However, expansion during discharge cannot be measured by this method since the true density cannot be considered as constant.

Equation (2) gives the content of $PbSO_4$ (p_q') as a function of the charge passed; an analogous equation holds for the content of PbO_2 (p_q), where M_1 in the numerator is replaced by $-M_2$. The calculated values of p_q were in good agreement with the results of chemical analyses, while the agreement was less satisfactory for p_q'. The final content of PbO_2 decreased with diminishing discharge current to $25 \pm 1\%$ at 0.21 mA/cm^2; its initial content (in the charged state) was $94.5 \pm 0.3\%$, hence the limiting utilization of the active mass was $73.5 \pm 1\%$. The limiting capacity of 19.3 A h (at 0.39 mA/cm^2) divided by the theoretical value of 26.7 A h gives a utilization of 72.3%. At 0.21 mA/cm^2 the capacity was smaller (18.2 - 18.9 A h), apparently due to self-discharge. In this state of extreme discharge, the remaining lead dioxide was encapsulated by lead sulphate crystals [10] and so escaped further reduction.

The values of titrimetric porosity (referred to the active mass without the grid), V_p', were higher than the pycnometric ones by, on average, 0.14. This discrepancy may be explained by the fact that adsorption of sulphuric acid on lead dioxide [11] increases the quantity of the acid in the pores. If we assume only a monolayer, the surface concentration is about 4×10^{-9} mol/cm^2. If we assume an internal surface area of 6 m^2/g [12] or about 3×10^5 cm^2/cm^3, porosity $V_{p\,o} = 0.5$ and 5M H_2SO_4, then 1 cm^3 of electrode contains 0.001 2 mol of adsorbed acid and 0.002 5 mol of acid in the liquid phase. Hence, the titrimetric porosity values are likely to be considerably increased by adsorption of the acid.

The tortuosity factor of the pores (f_p) was evaluated, from conductivity measurements in 1M H_2SO_4, as 2.02 - 2.29 in the charged and 2.22 - 2.37 in

the discharged state. Thus, the change of the f_p value is only slight in spite of a considerable drop in porosity during discharge (Fig. 1). Similar values were found by Romanova and Selitski [13], who also evacuated the plates before the measurements.

Negative plates

The measured discharge times at current densities of 0.02, 0.05, 0.1, 0.2, and 0.3 A/cm^2 were 74.7, 22.1, 8.1, 3.0, and 1.6 min, respectively (averages from four measurements). These values appear to be too low in comparison with the calculated values [14] of 164, 42.5, 13.2, 4.0, and 2.0 min, even if we take into account that the plates were somewhat thinner (0.18 cm) than assumed in the calculations (0.2 cm) and make a correction for the grid. The most probable explanation is that the concentration of the expander used in our plates was too low. This was dictated by the desired charge acceptance of the plates at low temperatures.

To calculate the true density of the active mass, ρ_t, we denote the percentage of lead and lead sulphate, at a charge passed from the beginning of discharge, q, as p_q and p_q', respectively. Equation (1) applies, but ρ_2 now denotes the density of lead (11.34 g/cm^3), and p_q' is given by eqn. (2), where M_2 is replaced by the molar mass of lead (M_3); the initial content of PbSO$_4$ $p_o' = 3.3\%$, and $m_o = 0.474$ g/cm^2. The calculated dependence of ρ_t on the total charge per plate, C, is shown in Fig. 2.

The experimental points at $C < 5$ A h lie below the theoretical curve as a result of the oxidation of lead by air, which could not be prevented. The composition of the charged and dried negative plates was found to be 73.4 - 79.8% Pb, 13.2 - 22.5% PbO, and 1.9 - 4.7% PbSO$_4$. Assuming a mean composition of 76.8% Pb, 3.3% PbSO$_4$, and 19.9% PbO (tetragonal), the true
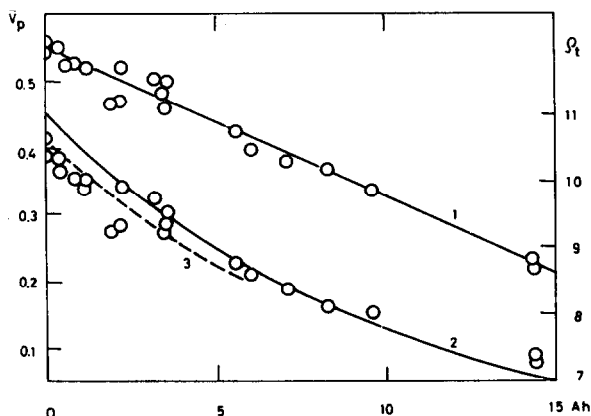

Fig. 2. Dependence of the mean porosity, $\bar{V}_p$ (1), and true density, ρ_t (2, 3), of negative plates on the charge passed. Straight line 1 corresponds to eqn. (7), curve 2 was calculated from eqns. (1) and (2) with $\rho_2 = 11.34$ g/cm^3 and M_2 the molar mass of lead, curve 3 involves a correction for the analytically found content of PbO.

density of the dried negative plates at the beginning of discharge was calculated as shown by the dashed curve in Fig. 2, which lies closer to the experimental points. If we assume, for a plate of the given mean composition and measured apparent density ρ_a = 4.70 g/cm^3, that the tetragonal lead(II) oxide is reduced to lead, we can calculate the corresponding increase in porosity as 0.021. This gives an idea of the slight changes of the porosity due to partial oxidation of lead in charged negative plates.

The dependence of the porosity, V_p, on the charge q is given by an expression similar to eqn. (3) but with an opposite sign before the parentheses. The correction for a grid of mass 0.251 g/cm^2 will be 0.251/10.78 = 0.023 cm, which must be subtracted from the plate thickness $2d$ = 0.18 cm to give $2d'$ = 0.157 cm. If the charge is expressed in A h, eqn. (3) takes the form

$$\bar{V}_p = V_{po} - 0.019\ 0C, \tag{6}$$

where C = 0.106 7q (A h). A series of measurements is shown in Fig. 2 (upper part); the points are fitted by a regression line of algebraic form (correlation coefficient -0.984)

$$V_p = 0.548 - 0.022\ 4C, \tag{7}$$

whose slope approaches theoretical. The measured initial porosity (average from two plates) is 0.553.

The expansion of a negative plate during discharge was found to be of a similar magnitude to that of a positive plate, $i.e.$, about 1 - 2%. Unlike the positive plate, the expansion was reversible ($2d$ = 0.239 cm after the second cycle, 0.235 cm after the tenth cycle). If the plate did not expand, its thickness in the discharged state would be lower by 1 - 2% and the factor of 0.022 4 in eqn. (7) would increase slightly to 0.022 6 - 0.022 8 ($cf.$ text below eqn. (5)). The scatter of the experimental points (Figs. 1 and 2, upper parts) is apparently due to the fact that the initial porosities of the tested plates were not all exactly the same.

The content of lead sulphate, p_q', as a function of q is given again by eqn. (2), but now M_2 refers to molar mass of lead rather than to lead dioxide. The negative plates contained 91 g of formed, dried, active mass and their surface area was 192 cm^2, hence, m_o = 91/192 = 0.474 g/cm^2. As a first approximation, we assume that the weight of the plate is not affected by the partial oxidation of lead by air, so that the combined content of lead and lead(II) oxide can be calculated approximately as

$$p_q = \frac{m_o p_o - 100 M_3 q/F}{m_o + (M_1 - M_3) q/F}, \tag{8}$$

where M_1 and M_3 denote molar masses of PbSO$_4$ and Pb, respectively, and p_o = 95%, the initial content of both Pb and PbO. The calculated values of p_q were in satisfactory agreement with the analytical results (within several percent), while the analytical data for p_q' again showed (as with the positive

plates) a rather large scatter, indicating that the analytical method used was not sufficiently reliable.

The plate capacities in the second cycle at a 20 h discharge rate were in the range 13.9 - 16.4 A h; capacities measured in another series in the 11th cycle were 14.7 - 16.1 A h, *i.e.*, they were less scattered. The "theoretical" capacity (at full conversion of the available lead) would be 22.4 A h, hence, the utilization of the active mass attained in the 11th cycle was 66 - 72%. Similar capacity values were measured at 10 - 100 h discharge rates (unlike positive plates), indicating that transport restrictions in the pores of negative plates are less important than those in positive ones, as was also shown on a theoretical basis [14].

The values of the titrimetric porosity, V'_p, corrected for the volume of the grid, were almost equal to those measured pycnometrically. This shows that, unlike positive plates, the adsorption of sulphuric acid does not play a role.

The values of the tortuosity factor, f_p, show a weak correlation with the porosity, $\bar{V}_p$. The regression line was calculated as

$$f_p = -3.046\bar{V}_p + 2.721 \tag{9}$$

in the interval $0.335 \leq \bar{V}_p \leq 0.546$ (correlation coefficient $r = -0.769$). Thus, at the end points of the given interval we have $f_p = 1.70$ and 1.06; the measured values (mean of two measurements) are 1.61 and 1.18. The drop in f_p with increasing $\bar{V}_p$ values is physically understandable [15] and is a fairly general phenomenon. The measured values of f_p are lower than for the positive plates probably owing to a more regular (homoporous) structure of the negative plates, which are, for this reason, less sensitive to transport restrictions. It is noteworthy in this respect that the mean pore radii of charged negative plates were found from mercury porosimetry [12] to be an order of magnitude larger, and the specific surface area an order of magnitude smaller, than for positive plates.

It should be noted that shortly after charging the plates, the values of f_p may be appreciably higher owing to gas bubbles trapped in the pores [13], however, the trapped gases are slowly removed — even if not quantitatively — by capillary forces; in our work they were removed by evacuation.

Conclusions

Density measurements support the conclusions of other workers [7, 8] on the presence of amorphous PbO_2 in positive plates. The porosity changes of positive lead accumulator plates during discharge are somewhat smaller than those theoretically predicted due, partly, to a slight expansion of the plates during discharge and partly to the probable presence of amorphous PbO_2. The plates undergo a contraction during charging, which is not quite reversible, resulting in a slight increase in volume from cycle to cycle. The values of the tortuosity factor suggest that the negative plates have a more regular porous structure with better transport properties than positive plates.

References

1 K. Micka and M. Svatá, J. Power Sources, 3 (1978) 167.

2 K. Micka and I. Roušar, Collect. Czech. Chem. Commun., 40 (1975) 921.

3 W. O. Butler, C. J. Venuto and D. V. Wisler, J. Electrochem. Soc., 117 (1970) 1 339.

4 Ch. D. Hodgman, (ed.), Handbook of Chemistry and Physics, Chem. Rubber Publ., Cleveland, Ohio, 1962, p. 594.

5 P. Ness, Electrochim. Acta, 12 (1967) 161.

6 H. Bode, H. Panesar and E. Voss, Chem. Ing. Tech., 41 (1969) 878.

7 P. Reinhardt, M. Vogt and K. Wiesener, J. Power Sources, 1 (1976) 127.

8 S. M. Caulder and A. C. Simon, J. Electrochem. Soc., 121 (1974) 1 546.

9 J. F. Dittmann and J. F. Sams, J. Electrochem. Soc., 105 (1958) 553.

10 A. C. Simon, C. P. Wales and S. M. Caulder, J. Electrochem. Soc., 117 (1970) 987.

11 I. G. Kiseleva and B. N. Kabanov, Dokl. Akad. Nauk SSSR, 122 (1958) 1 042.

12 M. Svatá, unpublished results.

13 I. L. Romanova and I. A. Selitskii, Elektrokhimiya, 6 (1970) 1 776.

14 K. Micka and I. Roušar, Electrochim. Acta, 21 (1976) 599.

15 P. Hugo, Chem. Ing. Tech., 46 (1974) 645.