

## Analysis of positive-plate resistance during cycling and the effect of compression

M. Calábek<sup>a</sup>, K. Micka<sup>b,\*</sup>, P. Bača<sup>a</sup>, P. Křivák<sup>a</sup>, V. Šmarda<sup>a</sup>

<sup>a</sup> Technical University of Brno, Antonínská 1, 662 09 Brno, Czech Republic

<sup>b</sup> J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague, 8, Czech Republic

Received 30 September 1996; accepted 12 December 1996

### Abstract

An electrochemical cell is designed and constructed to enable in situ measurements of the resistance of both the active mass and the interphase between the current-collector and the active mass in lead/acid test electrodes during cycling at well-defined degrees of compression ranging from zero to 90 kPa. Preliminary results of measurements on positive electrodes are well reproducible and show that, after conditioning cycles, both the interphase resistance and the active-mass resistance are independent of compression. Time changes of the two resistances are also studied and discussed. © 1997 Published by Elsevier Science S.A.

### 1. Introduction

Previous studies [1,2] in the authors' laboratories have been mainly concerned with repetitive charge/discharge cycling of positive plates with specially prepared grids made from various lead alloys. The electrodes were cycled under the so-called 'bad regime', characterized by slow charging (taking approximately 18 h) that gives a short cycle life, and under the so-called 'good regime', distinguished by charging at a substantially higher rate. It was found that the discharge capacity of the test electrodes under the bad regime is related with the active-material conductance in the charged state, but not with that of the grid/active-material interphase. The correlation between the charged active-material conductance and the discharge capacity measured under the good regime is complicated by the effect of the grid-alloy composition. The interphase resistance values for the individual ribs show a scatter that becomes very pronounced at the end of the cycle life. This indicates a degradation of the porous electrode structure that is often manifested by softening and shedding of the active material [2].

Observations related to the active-material degradation have been made by a number of authors. It is well known that porous oxide battery electrodes, including positive

lead/acid plates, undergo expansion (i.e., decrease of apparent density) [3,4] during cycling due to unequal molar volumes of the oxidized and reduced forms of the active material. With loosely arranged electrodes, the volume changes during discharging and recharging, although very small and difficult to measure, cause irreversible gradual expansion of the active material [5]. This phenomenon has been especially clearly demonstrated for plastic-bonded nickel hydroxide electrodes [6], where it was also shown that the thickness oscillations can be made reversible by applying compression of about  $0.5 \text{ kg cm}^{-2}$  (50 kPa).

Lead dioxide electrodes are different in that the product of reduction does not form a solid solution with the oxidized form but is precipitated in the pores in the form of separate crystals. Therefore, the changes in electrode volume (thickness) in this case are less reproducible than with nickel hydroxide electrodes, they are related not only to the molar volumes of  $\text{PbO}_2$  and  $\text{PbSO}_4$  but also to the mode of cycling, cycle number, etc. Nevertheless, a distinct tendency in thickness fluctuations of lead dioxide electrodes towards larger thickness was found during cycling [5]. It was shown later [7] that the thickness increase during cycling could be suppressed by applying compression of  $0.4\text{--}1 \text{ kg cm}^{-2}$  (40–100 kPa) to the plate assembly.

The question whether the positive electrodes expand on discharge and shrink on charge could not be decided unambiguously, as can be seen from the various results of measurements by different authors. Pavlov and Bash-

\* Corresponding author.

tavelova [8] found, in agreement with earlier work [5], expansion on discharge (and shrinkage on charge) which seems plausible; according to Atlung and Zachau-Christiansen [9], there was expansion on discharge and no change on charge during initial cycles, but later contraction on discharge and slight expansion on charge, although the behaviour was rather erratic. Bashtavelova and Winsel [10] deduced (from their somewhat complicated measurements) that discharge, unexpectedly, brings about shrinkage, and vice versa. Nevertheless, there is general agreement that the plate thickness increases slowly during the course of prolonged cycling, which, of course, leads inevitably to a progressive decrease in both the mechanical strength and the electrical conductance of the active mass. Degradation of the positive plate structure is often manifested by the formation of a sediment or mud at the bottom of the battery casing; it consists mainly of  $\text{PbO}_2$ . This is obviously formed at the end of charging during oxygen evolution and, as Atlung and Zachau-Christiansen [9] pointed out, it does not cause shorting between the plates.

Since the progressive expansion of the positive (as well as negative) plates can be stopped by applying compression to the whole electrode stack, many authors have followed this idea with the aim to employ it practically. For example, Feder and Biagetti [11] and Biagetti and Luer [12] designed and constructed a long-lived lead/acid battery with disk-shaped, compressed electrodes and pure-lead current collectors for prolonged float service. Alzieu and co-workers [13,14] studied the influence of compression on cycle life, especially during deep cycling. Up to 3000 cycles were thus attained at an optimum compression of about 800 kPa (higher pressures caused mechanical damage to both the electrodes and separators). Thorough measurements of both the pressure and the temperature in the battery revealed that the pressure increased during charging and decreased during discharging (which seems to contradict the results of Takahashi et al. [7] but to support those of the German authors [10]). Alzieu et al. [14] attributed this phenomenon to the effect of the temperature, which increased during charging and decreased during discharging. When the temperature in the battery was kept constant, the pressure behaved as expected, i.e. it decreased during charging and increased during discharging. These results are in accordance with the earlier measurements of the plate thickness [5,8] and they may also explain the anomalous findings of certain authors [9,10].

Some authors applied compression without a quantitative study and found a positive influence on the cycle life. Atlung and Zachau-Christiansen [9] stated that the cycle life of their experimental battery containing Pb–Ca–Sn grids could be increased by applying compression above 14 kPa. Tsubota et al. [15] proposed compressed, valve-regulated lead/acid batteries for automotive applications under deep-discharge duty; these batteries attained 1000 to 2000 cycles. Valeriotte et al. [16] used in their rather extensive work a slight but equal compression during deep

cycling of their battery containing expanded Pb–Ca–Sn grids to prolong the cycle life above 90 cycles. Finally, Landfors [17] used, in practically oriented and promising work, a constant compression of 100 kPa without attempting to find an optimum value; the cycle life of his experimental battery with triple-layered separators and lead grids containing 2.5 wt.% Sb increased from 90 to 1150 cycles at 75% depth-of-discharge.

Many authors have attempted to prevent the shedding of active material by suitable additives. Thus, Weininger and Secor [18] proposed polymer-bonded negative electrodes and the addition of carbon fibres (performing better than glass fibres) into the positive active mass [19]. Babayeva et al. [20] investigated the addition of polypropylene fibres; this principle was reviewed by Dasoyan and Aguf [21]. Lead accumulator electrodes with active mass containing synthetic fibres were patented [22]. The experimental results showed a favourable influence of various fibres on the mechanical strength of the electrodes and, thus, also on their cycle life [19,20].

## 2. Apparatus for studies of the effect of compression

### 2.1. Experimental cell

The experimental cell for measurement of the influence of compression on the resistance of the active mass and on the contact resistance between the current-collector and the active mass during operation of the test electrodes was designed, constructed, and tested in several variants. These variants differed in both their constructional details and the material used. The final variant is shown schematically in Fig. 1. Parts of the cell were manufactured from poly(vinyl chloride) (Novodur, made in Czech Republic), except for those indicated below.

The test electrodes (with a current-collector that consisted of parallel, mutually isolated ribs) have, in contrast to those used in earlier work [1,2], prolonged epoxy resin strips that are provided with four openings (Fig. 2) through which the leading rods (6) (Fig. 1) pass to ensure a stable position of the electrode within the cell. The collectors were prepared by using specially manufactured dies. The counter electrodes (2) have the same shape and dimensions as the test electrode.

The electrodes are separated by two fritted glass spacers (3) (Fig. 1) of 22 vol.% porosity held in a frame by pivots and transferring the pressure to the test electrode. The spacers were manufactured to this purpose in Kavalier Glass Works (Czech Republic) from chemically resistant Simax glass. A certain clearance between the frame with the spacer and the non-active parts of the electrodes permits a uniform compression over the whole active surface even if the contacting surfaces are not exactly coplanar. Projections on the base (4) and cover (5) plates (Fig. 1), placed against the active parts of the counter electrodes, prevent

pressing out of the active mass into the free space at high pressures.

The upper surface of the cover plate (5) (Fig. 1) is provided with a circular slit into which a cylindrical insert (7) fits, protruding above the electrolyte level. The insert transfers the pressure exerted by cylindrical weights of hard lead (8 and 9), placed above the electrolyte level. The weights fit into one another as well as into the cylindrical insert, ensuring the compression to be directed exactly vertically. Thus the degree of compression can be set in the range from 0.25 to 10 kg weight (1 kg weight equals approximately 9.8 N). Since the geometrical surface area of the test electrode equals  $2 \times 5.4 = 10.8 \text{ cm}^2$  (compare Fig. 2), 1 kg weight corresponds approximately to a compression of 9 kPa.

## 2.2. Electrodes and method of measurement

The current-collector of the test electrodes consists of ten, isolated, parallel ribs with an epoxy resin frame (see Fig. 2) and was pasted with industrial positive paste. The composition of the current-collector was Pb–1.6wt.%Sb–0.37wt.%Sn (denoted as Pb–Sb-1 in our previous reports [1,2]). The counter electrodes were prepared similarly except that all their ribs were short-circuited; they were provided with a single current lead and a lead for potential measurements. Investigations of the time effect without compression were performed on other electrodes that used collectors of the composition Pb–0.08wt.%Ca–0.6wt.%Sn.

The electrodes were formed in an excess of electrolyte (after 1 h soaking in  $\text{H}_2\text{SO}_4$  of density  $1.24 \text{ g cm}^{-3}$ ; this

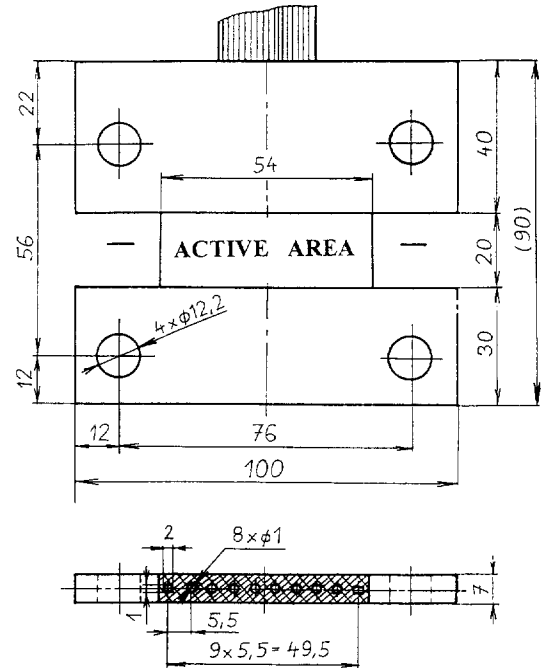


Fig. 2. Schematic view of the test electrode prepared by pasting a specially designed current-collector with isolated parallel ribs. A flat, 18-core cable (on top) serves as the current lead. The counter electrode has a similar design.

acid was also used in cycling) by an alternate series of 4 h charging with a current of 200 mA, 2 h standing, and so on; in total, 72 h charging and 36 h standing. Three conditioning cycles were applied and consisted of discharging at 210 mA to 1.6 V and charging at the 10 h rate

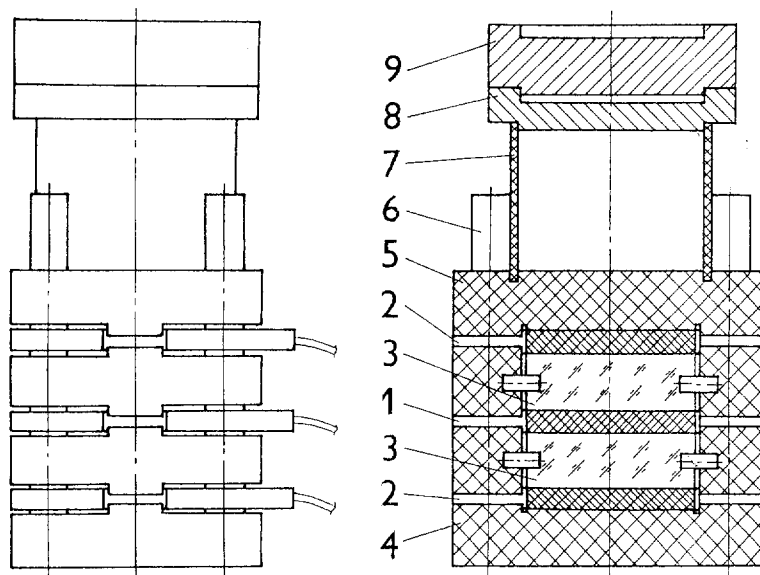


Fig. 1. Experimental cell for measurement of the influence of compression on the active mass and contact resistances of lead/acid electrodes during operation. Left: lateral view of the cell assembly. Right: perpendicular cross section. (1) test electrode; (2) two counter electrodes; (3) two porous glass inserts; (4) base; (5) pressing plate; (6) leading rods; (7) spacing insert; (8), (9) exchangeable weights.

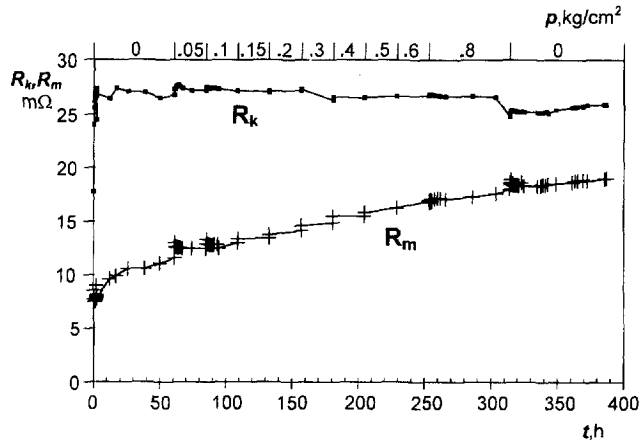


Fig. 3. Mean resistance of the active mass,  $R_m$ , between neighbouring ribs and mean contact resistance,  $R_k$ , of particular ribs of the current-collector at a compression that gradually increases from 0 to 0.8 kg cm<sup>-2</sup> during the time indicated.

to 125% of the measured capacity. In the fourth cycle, the electrodes were charged at a constant voltage of 2.40 V for 13 h.

To start the measurement, the electrodes were discharged at 0.45 A to 1.6 V to determine their capacity, then charged at a constant voltage of 2.4 V for 15 h to suppress gas evolution (the electrodes were in a horizontal position), and the evolution of the  $R_k$  and  $R_m$  values was followed for 60 h (without compression). Afterwards, the compression was increased gradually every 24 h up to 0.8 kg cm<sup>-2</sup>, while the resistances were measured immediately before and after the weight change (and sometimes in between). Finally, the weights were removed and the measurements continued for three days to see whether the resistances would change with the time.

In further experiments, the time effects were followed at various discharge states for 50 h in an excess of

electrolyte without compression. Prior to changing the state-of-discharge, a conditioning cycle was applied, i.e., 5 h discharge to 1.6 V (versus negative plate with excess capacity), return of 125% of the charge obtained, and partial discharge to the desired level.

The free-standing test electrodes measured in previous work [1,2] had to be taken out of the electrolyte for short-time intervals during every resistance (in fact, potential response) measurement to eliminate the time effect in charging the electrode double-layer of a relatively very high capacity; this phenomenon has been discussed in detail in Ref. [23] and has been used to determine the capacity of the electrode double-layer [24,25]. In the present case, removing the test electrode from the cell during every resistance measurement would present considerable difficulties. Fortunately, the fritted glass spacers of relatively low porosity (22 vol. %), causing an increase of the electrolyte resistance in the interelectrode space, lead to diminution of the mentioned time effect so that (if a small systematic error of about 2% is taken into account) it is possible to measure the potential response only 10 s after the measuring current is switched on. This time lag leads to increasing the total time of measurement on all electrode sections from about 1 to 5 min. The computer program was adapted accordingly.

### 3. Results

To test the newly constructed cell, a series of resistance measurements was performed at gradually increasing compression of the electrodes from zero to 0.8 kg cm<sup>-2</sup> (approximately 80 kPa). The results are shown in Fig. 3. It can be seen that the value of  $R_k$  increases only during the first few hours and then remains fairly constant, even when

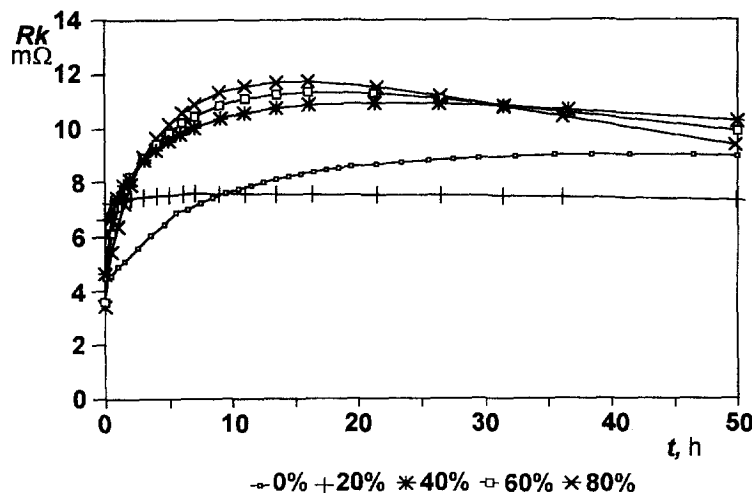


Fig. 4. Dependence of mean values of  $R_k$  on time elapsed from end of charging or discharging. The degree of discharge (%) is indicated for each particular curve.

the compression is gradually increased. On the other hand, the value of  $R_m$  increases constantly during the whole run, although gradually more and more slowly. Similar behaviour was observed in earlier work (where also an antimonial lead grid was employed) [26] during the course of 3000 h and it was attributed to a slow corrosion process of lead dioxide particles (i.e., to formation of a lead sulfate film due to slow self-discharge).

To supplement these observations, the time effect was studied without compression in the experimental set-up used earlier (i.e., in an excess of electrolyte without the porous glass separators). The evolution of the contact resistance and of the active-mass resistance during 50 h at various degrees of discharge beginning from zero and ending at 80%, is shown in Figs. 4 and 5, respectively. The curves corresponding to the fully charged state are similar to those in Fig. 3 if the first 50 h are considered. Hence, it appears that they are not much affected by the construction of the cell used. The initial rise of the  $R_k$  values indicates that the electrode after switching off the current is not really in a current-less state, since gradients of the electrolyte concentration in the pores give rise to potential gradients and, thus, to internal currents. Sites with a higher acid concentration have a more positive potential and function as cathodes (forming lead sulfate) with respect to those with a lower acid concentration, which function as anodes. Thus, if a higher acid concentration exists at the current-collector, rather than at a distance from it, it could be the reason for the slow formation of additional lead sulfate crystals in the interphase and cause the contact resistance to rise somewhat. Given the history (cycling, etc.) of the electrodes, however, it would be difficult to estimate the concentration relations in the pore electrolyte.

The changes of the  $R_k$  and  $R_m$  values during discharge-

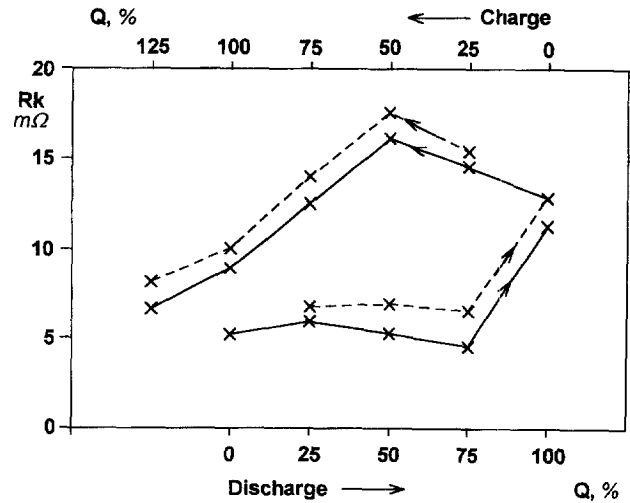


Fig. 6. Evolution of the mean values of  $R_k$  during discharge/charge cycle.

ing and charging an electrode are shown in Figs. 6 and 7, respectively. Here, the current was interrupted for an hour at 1 h intervals; the resistances were measured both at the beginning (points joined by solid line) and the end of the 1 h break (points joined by dashed line). The electrode was discharged at a 4 h rate (to 1.6 V versus negative Pb electrode) and after 1 h break it was charged with the same current for 5 h (i.e., with 125% overcharge).

The pronounced hysteresis of the curves in Fig. 6 is obviously due to the time effect shown in Fig. 4: during each 1 h break, the value of  $R_k$  increases somewhat; and this time effect is also operating during charging, where it initially overcompensates the decrease of  $R_k$  caused by oxidation of lead sulfate to lead dioxide. The shallow

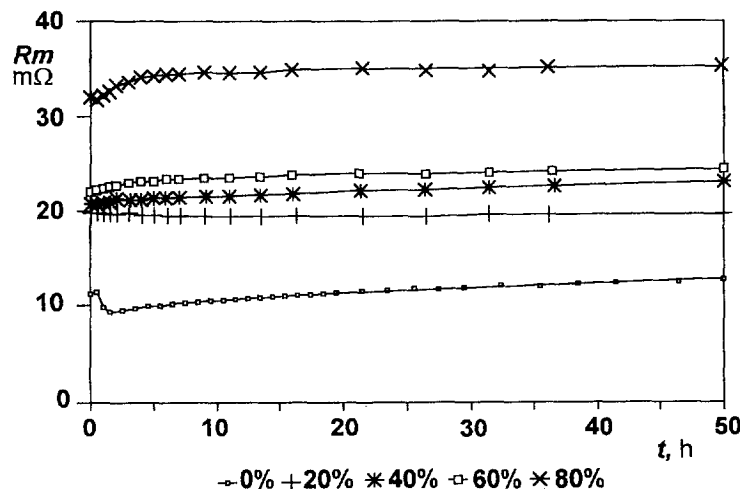


Fig. 5. Dependence of mean values of  $R_m$  on time elapsed from the end of charging or discharging. The degree of discharge (%) is indicated for each particular curve.

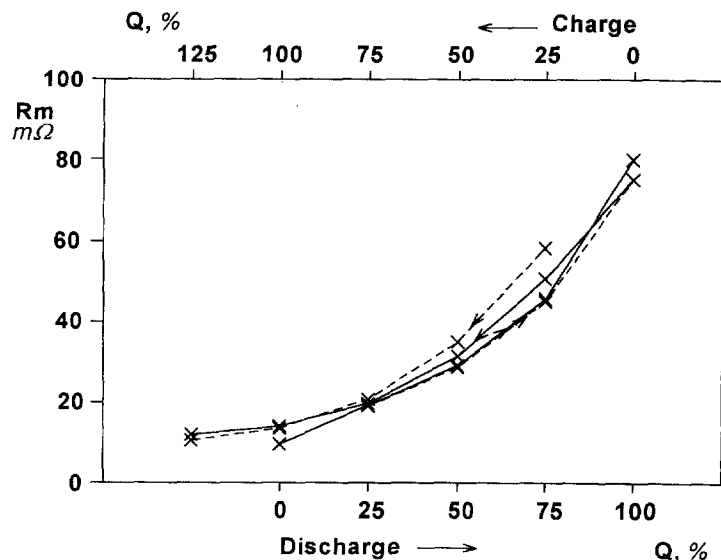


Fig. 7. Evolution of the mean values of  $R_m$  during discharge/charge cycle.

minimum of the contact resistance during discharging was also observed in earlier work [27], where it was attributed to a pressure increase caused by the voluminous lead sulfate.

On the other hand, the curves in Fig. 7 show practically no hysteresis, in keeping with the negligible time effect illustrated in Fig. 5.

To investigate the effect of compression during long-term cycling experiments, especially from the point of view of the cycle life and previous studies using no compression [1,2], further work will be necessary.

#### 4. Conclusions

A new electrochemical cell has been designed and constructed. It enables reliable, in situ measurements of the active-mass resistance,  $R_m$ , interphase resistance,  $R_k$ , and capacity of laboratory electrodes during cycling under various degrees of compression. Preliminary measurements have shown that both the values of  $R_m$  and  $R_k$  of positive electrodes that are subjected to a limited number (about 15) of deep cycles are independent of the degree of compression ranging from zero to  $0.8 \text{ kg cm}^{-2}$  (80 kPa). The  $R_m$  values increase slowly with time over periods of hundreds of hours, whereas the  $R_k$  values increase appreciably only during the first few hours.

#### Acknowledgements

The authors are indebted to František Kořínek and ing. Libor Šácha for careful technical assistance. This work was supported by the Advanced Lead–Acid Battery Con-

sortium (in Project No. AMC-010), a program of the International Lead Zinc Research Organization, and by the Grant Agency of the Czech Republic (Grant No. 12/96/0963).

#### References

- [1] M. Calábek, K. Micka, P. Bača, P. Křivák and V. Šmarda, *J. Power Sources*, in press.
- [2] M. Calábek, K. Micka, P. Bača, P. Křivák and V. Šmarda, *J. Power Sources*, in press.
- [3] J.F. Dittmann and J.F. Sams, *J. Electrochem. Soc.*, 105 (1958) 553.
- [4] E.J. Ritchie and J. Burbank, *J. Electrochem. Soc.*, 117 (1970) 299.
- [5] K. Micka, M. Svatá and V. Koudelka, *J. Power Sources*, 4 (1979) 43.
- [6] K. Micka, J. Mrha and B. Klápště, *J. Power Sources*, 5 (1980) 207.
- [7] K. Takahashi, M. Tsubota, K. Yonezu and K. Ando, *J. Electrochem. Soc.*, 130 (1983) 2144.
- [8] D. Pavlov and E. Bashtavelova, *J. Electrochem. Soc.*, 133 (1986) 241.
- [9] S. Atlung and B. Zachau-Christiansen, *J. Power Sources*, 30 (1990) 131.
- [10] E. Bashtavelova and A. Winsel, *J. Power Sources*, 46 (1993) 219.
- [11] D.O. Feder and R.V. Biagetti, *Bell Lab. Rec.*, 50 (1972) 207; *Chem. Abstr.* 77 (16) (1972) 504.
- [12] R.V. Biagetti and H.J. Luer, *J. Power Sources*, 4 (1979) 309.
- [13] J. Alzieu and J. Robert, *J. Power Sources*, 13 (1984) 93.
- [14] J. Alzieu, N. Koehlin and J. Robert, *J. Electrochem. Soc.*, 134 (1987) 1881.
- [15] M. Tsubota, S. Osumi and M. Kosai, *J. Power Sources*, 33 (1991) 105.
- [16] E.M.L. Valeriotte, A. Heim and M.S. Ho, *J. Power Sources*, 33 (1991) 187.
- [17] J. Landfors, *J. Power Sources*, 52 (1994) 99.
- [18] J.L. Weininger and F.W. Secor, *J. Electrochem. Soc.*, 121 (1974) 1541.
- [19] J.L. Weininger and C.R. Morelock, *J. Electrochem. Soc.*, 122 (1975) 1161.

- [20] L.N. Babaeva, V.G. Vasilev, P.I. Dozortseva, K.V. Ruts kaya, N.M. Emelyanov and V.S. Smolkova, *Sbornik rabot khim. istochnikam toka, Leningrad*, 10 (1975) 96.
- [21] M.A. Dasoyan and I.A. Aguf, *Sovremennaya teoriya svincovogo akkumulyatora*. Izdat. Energiya, Leningrad, 1975, pp. 149–154.
- [22] J.P. Cestaro and U. Sokolov, *US Patent No. 3973991, Cl. H01M 35/08* (1976); *Chem. Abstr.*, 86 (2) (1977) 92.
- [23] M. Calábek and K. Micka, *Proc. Advances in Lead– Acid Batteries*, Vol. 84–14, The Electrochemical Society, New Orleans, 1984, p. 288.
- [24] K. Micka and I. Roušar, *Electrochim. Acta*, 32 (1987) 1387.
- [25] M. Calábek and K. Micka, *Electrochim. Acta*, 33 (1988) 75.
- [26] M. Calábek and K. Micka, *J. Power Sources*, 30 (1990) 1309.
- [27] M. Calábek and K. Micka, *Electrochim. Acta*, 37 (1992) 1805.