Journal of Applied Electrochemistry **34**: 1113–1118, 2004.

Studies of current and potential distributions on lead-acid batteries. II. Discharge of automotive negative plates

YI LI, GUODONG ZHANG and YONGLANG GUO*
Department of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P.R. China
*(*author for correspondence, e-mail: yguo@sdu.edu.cn)*

Received 8 March 2004; accepted in revised form 6 June 2004

Key words: current and potential distributions, lead-acid batteries, negative plate

Abstract

The distributions of current density and potential of automotive negative plate were studied by measuring the *IR* drop in the H_2SO_4 solution between the positive and negative plates. At the beginning of discharge, the distributions of current density, potential and polarization resistance are uniform. In the later stage, high polarization appears at the top and bottom of the negative plate and the current density falls very quickly in these regions. Therefore, high polarization resistance of the active mass increases very quickly at both the top and bottom of the negative plate. It is mainly caused by the passivation of the negative plate which obviously decreases by constant current charge. At low temperature, at the end of 3 C discharge, the highest polarization and the lowest current density appear farthest away from the lug and at the top of the negative plate.

1. Introduction

Although the lead-acid batteries have been widely used in many applications, the utilization of its active mass is still relatively low, especially at a high discharge rate. It is well known that the active mass utilization, as well as the performance of lead-acid batteries, is affected by uneven current and potential distributions over the plate surfaces. Researchers have used a variety of methods to measure these distributions. Asai et al. [1] calculated the potential and current distributions of tall tubular positive plate under discharge on the basis of the plate resistance and the current-potential-time relationship. Sunu et al. [2] obtained the current density distribution by measuring grid voltage drop and electrode polarization. Král et al. [3, 4] determined the current distribution over the plate surfaces in the course of discharge mathematically by using the equivalent circuit method. In our previous work [5, 6], the distributions of current density and potential over the positive plate surfaces were investigated by measuring the *IR* drop in the H_2SO_4 solution between the positive and negative plates.

Studies of the distributions of current density and potential in lead-acid batteries have mainly focused on the grid and the positive plates [1–12]. Little attention has been paid to the negative plates. The objective of this work is to study the distributions of current density and potential on automotive negative plates by measuring the *IR* drop in the H_2SO_4 solution between the positive and negative plates under discharge so as to further understand the negative plate behavior.

2. Experimental

The test plates were commercial automotive plates produced by the Jin Fengfan Storage Battery Co., Ltd (China). The negative grid used was of conventional orthogonal design with dimensions of 14.3 cm (W) × 12.5 cm (H) × 0.13 cm (T) and about 80 g active mass on each negative plate. The thickness of the pasted negative plate was 0.16 cm. In charge-discharge cycles, the negative plate was placed between positive plates. To ensure that the capacity of the cell was determined by the negative plate, two positive plates were placed on each side of the negative plate. The distance between the positive and negative plates was about 4.5 cm. (Figure 1). The container had internal dimensions of 14.3 cm (W) × 15.0 cm (H) × 10.0 cm (L). In order to ensure parallel ion flow between the negative and positive plates, the width of the container and the height of the H_2SO_4 electrolyte were the same as the dimensions of the automotive negative plate. The acid density was 1.285 g cm^{-3}. Since there is excess H_2SO_4 electrolyte under the experimental conditions, complete discharge leads to a H_2SO_4 concentration decrease of only about 1%. The local current density on the surface of the negative plate could be obtained by measuring the *IR* drop in the H_2SO_4 electrolyte between the negative

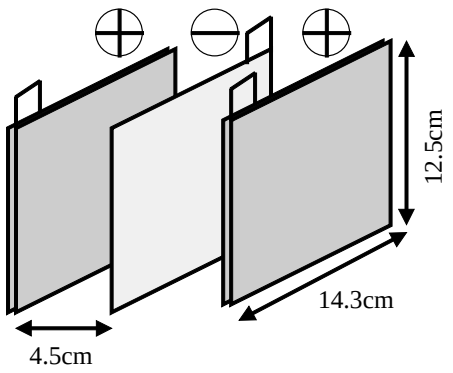

Fig. 1. Arrangement of plates.

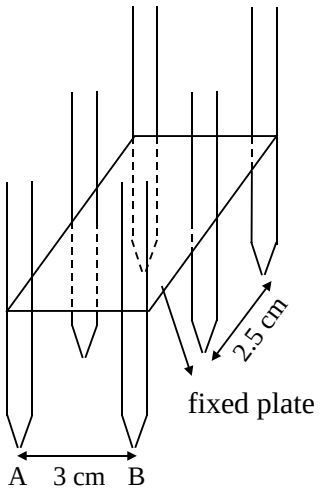

Fig. 2. Arrangement of three pairs of reference electrodes.

and positive plates through a pair of $Hg/Hg_2SO_4/H_2SO_4$ (1.285 g cm^{-3}) reference electrodes during discharge. One of the reference electrodes was placed close to the negative plate and was used to measure the negative electrode potential. The potentials reported in this experiment were measured against the reference electrode above. Figure 2 shows the reference electrode arrangement. Three pairs of parallel reference electrodes with 2.5 cm spacing were used. The distance between points A and B was 3 cm and the outer diameter of the reference tip was about 0.15–0.20 cm. When the three pairs of reference electrodes moved from the bottom to the top twice, we could measure the distributions of current and negative electrode potential on the entire negative plate surface by recording the IR_{AB} drop and the potentials.

At room temperature (20 ± 2 °C), wet-charge of the negative plate was discharged at 36 and 9 A, respectively. In order to investigate the cold cranking ability (CCA), the plate was discharged at −18 °C. The data were recorded with a HP 34970A Data Acquisition/Switch Unit connected to a PC.

3. Results and discussion

3.1. *Distributions of current density and potential at high discharge rate (3 C)*

When a positive plate was discharged at 36 A (3 C rate), the discharge capacity was only 3.9 Ah [5]. Under the same conditions, the discharge capacity of the negative plate was 4.6 Ah at the terminal potential of −0.8 V. Since the capacity of the negative plate was higher than that of the positive plate, we used four positive plates as the counter electrodes. In other words, two positive plates were placed on each side of the negative plate (Figure 1).

In order to obtain the current density distribution on the negative plate, we assume that the electrolyte resistance up and down the battery is uniform during the scan of reference electrodes from the bottom to the top of the negative plate. Therefore, the voltage drop measured by two opposite reference electrodes is proportional to the current through the electrolyte. The current density on the negative plate can be calculated using the following equations:

$$\frac{U}{\sum U} = \frac{IR}{\sum IR} \tag{1}$$

$$i = \frac{18 \times U}{1.146 \times \sum U} \tag{2}$$

where i denotes the current density on the negative plate; U, the IR voltage drop in the H_2SO_4 electrolyte between each pair of reference electrodes; and R the electrolyte resistance. Since the automotive negative plate was discharged at 36 A (3 C rate), the current on each side of the plate was 18 A. Three pairs of reference electrodes were moved from the bottom to the top of the negative plate twice and the IR drop was measured at each 0.5 cm in height, so we altogether recorded 156 potential differences and 156 electrode potentials on the negative plate. If we divide the negative plate into 156 measurement points, I is the current intensity over an area of 1.146 cm^2 on the negative plate.

When the negative plate was discharged at 36 A (3 C rate) for 1, 4, 6 and 7 min, the distributions of potential and current density were measured. Figure 3 shows the current density distribution of the negative plate at the discharge time of 1 min. High current density appears close to the lug and around the grid frame. This is due to the low grid resistance in these regions. Moreover, the current density in the lower part of the negative plate was higher than that in the middle. With discharge of the negative plate, the current density drops gradually at the bottom and top of the negative plate. Figure 4 shows the distribution of current density on an automotive negative plate at a discharge time of 7 min. At the end of discharge, the current density decreases greatly at the top and bottom of the plate, while it increases in the center. At the beginning of discharge, more active mass

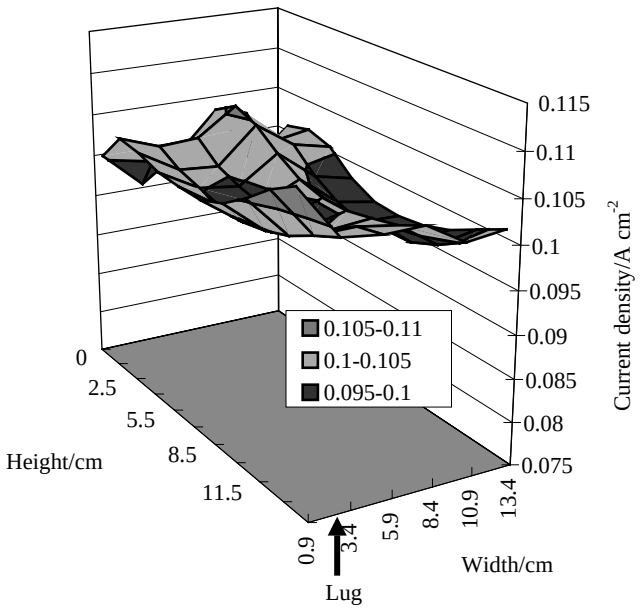

Fig. 3. Distribution of current density on an automotive negative plate during discharge at 36 A. Discharge time: 1 min.

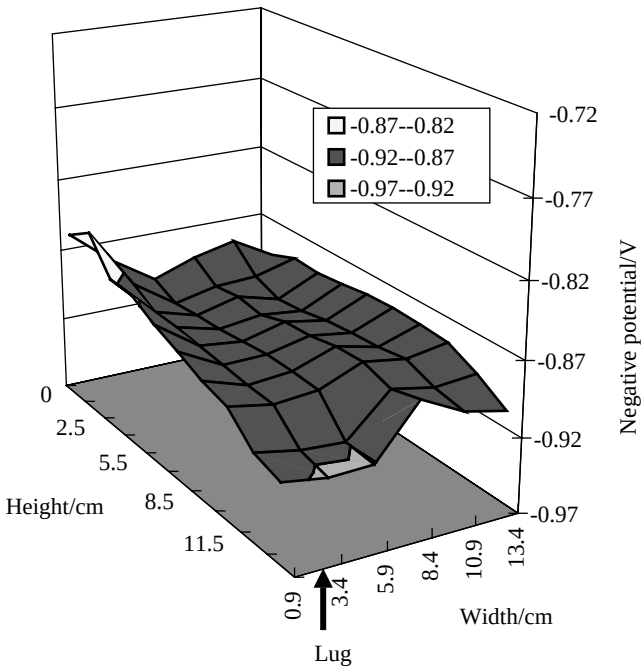

Fig. 5. Distribution of negative electrode potential on an automotive negative plate during discharge at 36 A. Discharge time: 1 min.

is consumed at the top of the negative plate because of the high current density in these regions, therefore, the current density decreases rapidly at the top of the negative plate. The undercharged region may appear at the bottom of the negative plate, which leads to rapid current density drop at the end of discharge. Because the total current intensity does not change, the current density in the middle of the negative plate increases with decreasing current density at the top and bottom.

H_2SO_4 electrolyte stratification causes the potential difference between the upper and lower parts of the plate on open circuit. In our experiment, the electrolyte was stirred with air for a few minutes before discharge. Therefore, the potential difference over the negative plate surface on open circuit was low and could be neglected. Since a large change took place in the potential at the beginning of discharge, the measurement of potential was carried out after 1 min discharge. Figure 5 shows the distribution of the negative electrode potential at a discharge time of 1 min. It is found that the distribution of potential is uniform on the negative plate, except for the low polarization around the lug. During discharge,

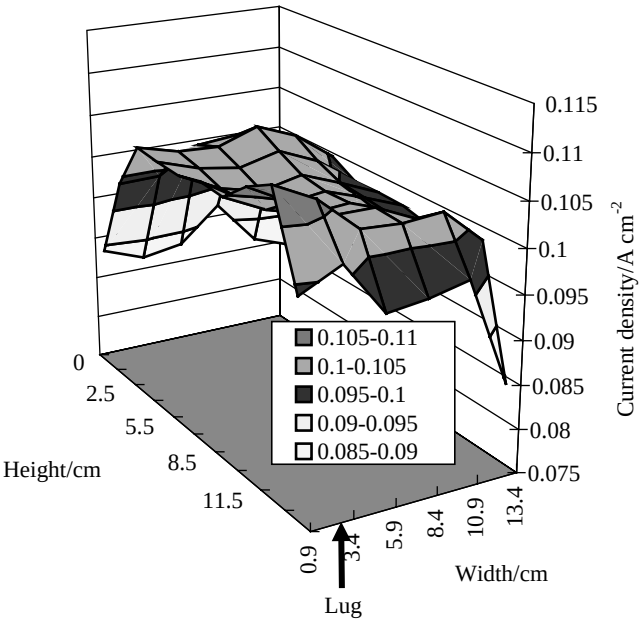

Fig. 4. Distribution of current density on an automotive negative plate during discharge at 36 A. Discharge time: 7 min.

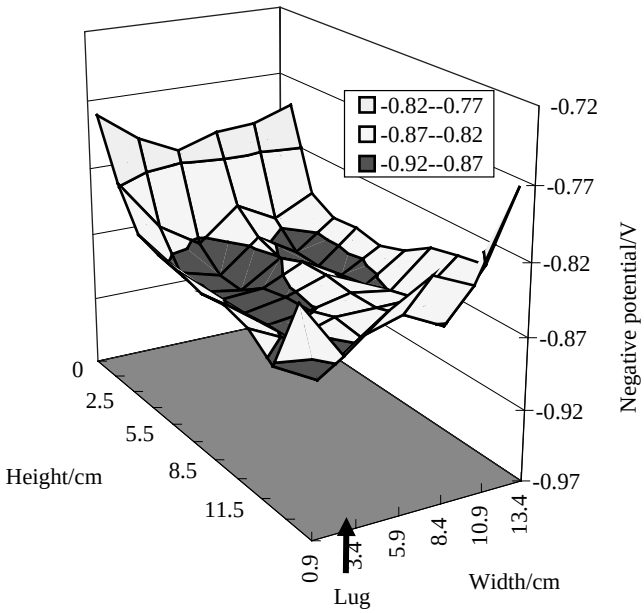

Fig. 6. Distribution of negative electrode potential on an automotive negative plate during discharge at 36 A. Discharge time: 7 min.

the polarization of the negative plate increases gradually, and the available area of the active mass decreases while the current density increases. Figure 6 shows the distribution of potential on the automotive negative plate at the end of discharge. The highest polarization occurs at the top and bottom of the plate. This is because at the beginning of discharge the high current density at the top leads to the consumption of more active mass. The deep discharge at the top and the undercharge at the bottom can result in passivation and high polarization in these regions. It is clear that this polarization will cause the negative plate discharge to stop.

When a negative plate is discharged, the polarization resistance is defined by the ratio of the polarization potential to the current density. Figures 7 and 8 show the distribution of resistance on negative plate at discharge times of 1 and 7 min, respectively. It is found that the resistance of the active mass increases very quickly at the top and bottom during discharge. This results in passivation in these regions.

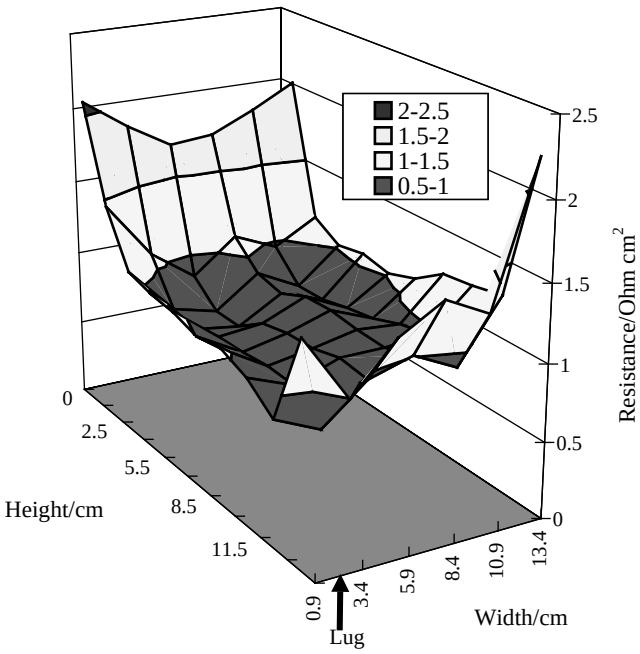

Fig. 8. Distribution of polarization resistance on an automotive negative plate during discharge at 36 A. Discharge time: 7 min.

3.2. *Passivation of the negative plate at high discharge rate (3 C)*

In order to study passivation of the plate, an automotive negative plate underwent deep discharge at 36 A (3 C rate). The discharge time was 10.7 min. After 8 min, the polarization increased quickly at the top. Figure 9 shows the distribution of the potential in the middle part of the plate in deep cycles under different charge conditions. High polarization appears in the upper part after deep discharge. At the beginning of discharge, the potential distribution is uniform and is about −0.9 V (see Figure 5), therefore, the change in polarization is about 400 mV at the top of the plate during the first deep discharge, while it is about 200 mV in the middle and lower parts. The results are similar to those obtained at the end of 9 A discharge (see Figure 10). The highest polarization appears at the top of the plate.

Under constant voltage charge, the polarization becomes increasingly higher in the upper part of the plate over the cycles (Figure 9), while the polarization in the lower part changes little. After six cycles of constant voltage charge, the polarization increases again by about 100 mV at the top of the plate. However, in the seventh cycle, the polarization decreases at the top. This

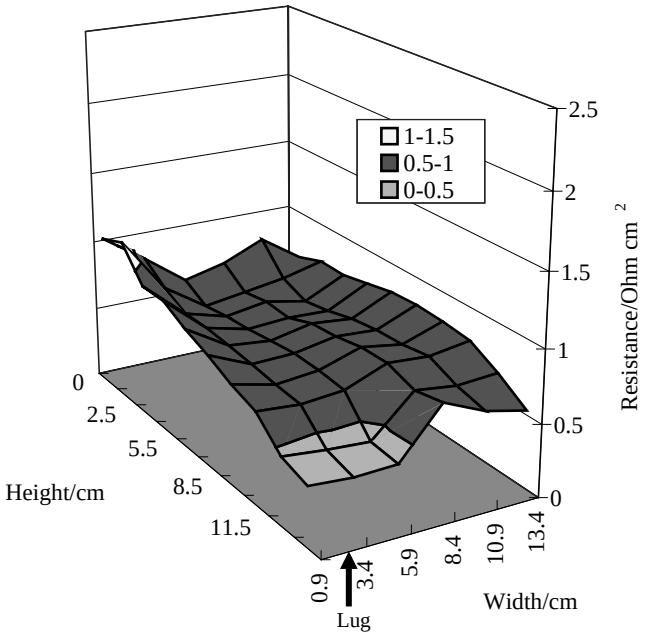

Fig. 7. Distribution of polarization resistance on an automotive negative plate during discharge at 36 A. Discharge time: 1 min.

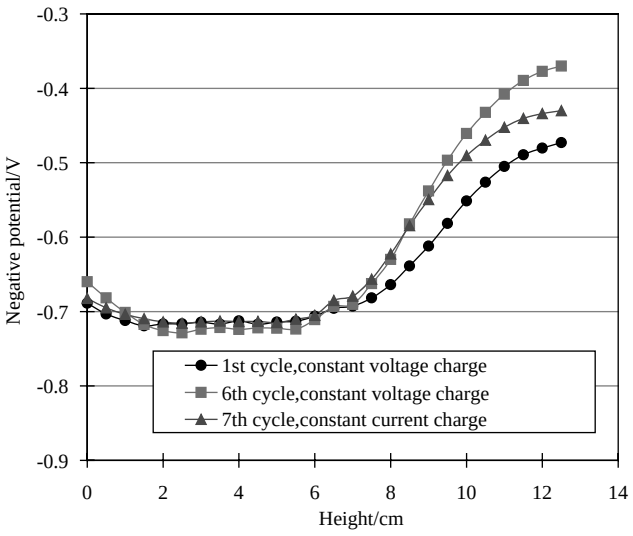

Fig. 9. Distribution of negative electrode potential in the middle of the negative plate in the deep cycles during discharge at 36 A. Discharge time: 10.7 min, Constant voltage charge: 2.5 V at 2.5 A limitation current for 6.5 h, Constant current charge: 2.5 A for 6 h.

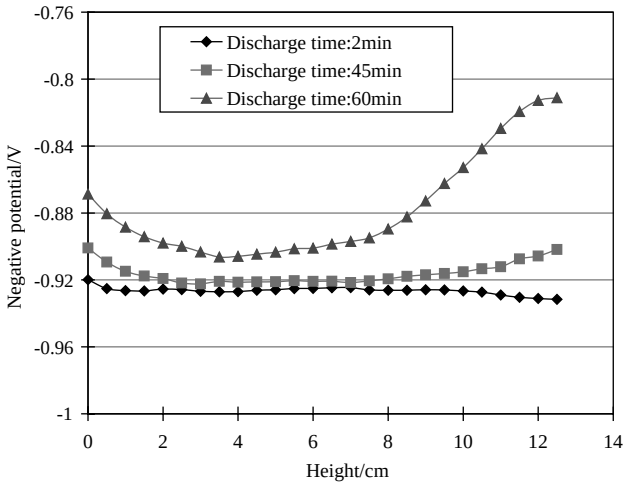

Fig. 10. Distribution of negative electrode potential in the middle of the negative plate at different discharge times. Discharge current: 9 A.

means that passivation decreases under constant current charge.

3.3. *Distributions of current density and potential at medium discharge rate (0.75 C)*

When the negative plate was discharged at 9 A (0.75 C rate), the distributions of potential and current density were measured at different discharge times. Figure 10 shows the change in the distribution of negative electrode potential in the middle part of the plate. It is found that the potential distribution is uniform at the beginning of discharge and becomes uneven near the end of discharge. The polarization increases greatly, especially at the top of the plate at the end of discharge. As a result, high polarization leads to serious passivation in these regions. Figure 11 shows the distribution of current density in the middle part of the plate. The current density changes little at the beginning of discharge. However, at the end of discharge, the current

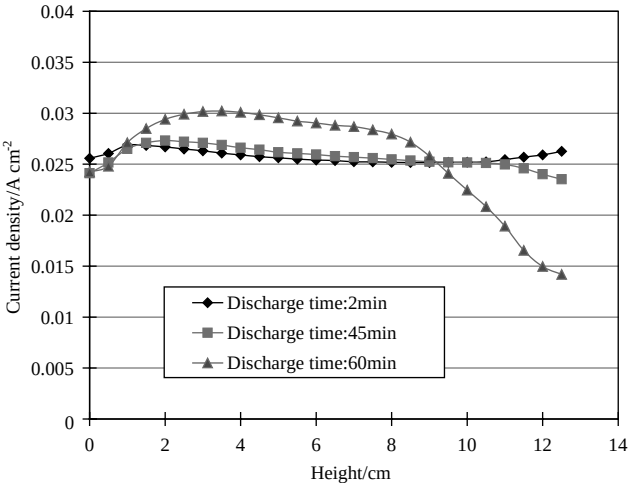

Fig. 11. Distribution of current density in the middle of the negative plate at different discharge times. Discharge current: 9 A.

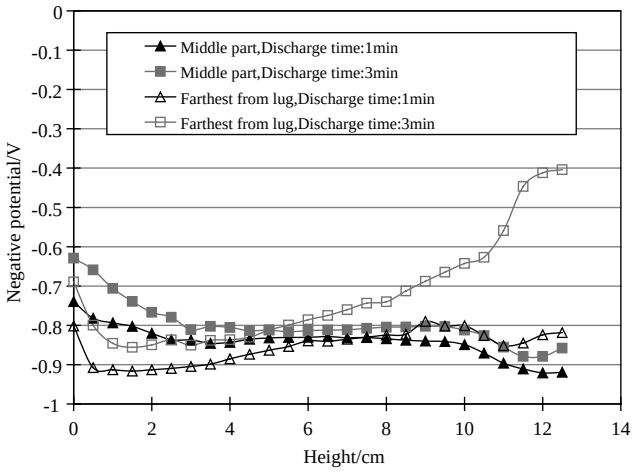

Fig. 12. Distribution of negative electrode potential in the middle of the negative plate and farthest from the lug. Discharge current: 36 A. Temperature: −18 °C.

density falls quickly at the top, while it increases in the middle of the plate because the discharge current of is unchanged.

3.4. *Distributions of potential and current density at low temperature*

At low temperature, the cold cranking ability of the negative plate is very important to an automotive lead-acid battery. When the plate was discharged at 36 A (3 C rate) at −18 °C, the distributions of potential and current density were measured at discharge times of 1 and 3 min. Figure 12 shows the distribution of the potential in the middle part of the plate and at the points farthest from the lug. It is found that the polarization in the middle part changes little during discharge. However, the highest polarization appears at the points farthest from the lug and at the top. The change in polarization is about 400 mV. Figure 13 shows the

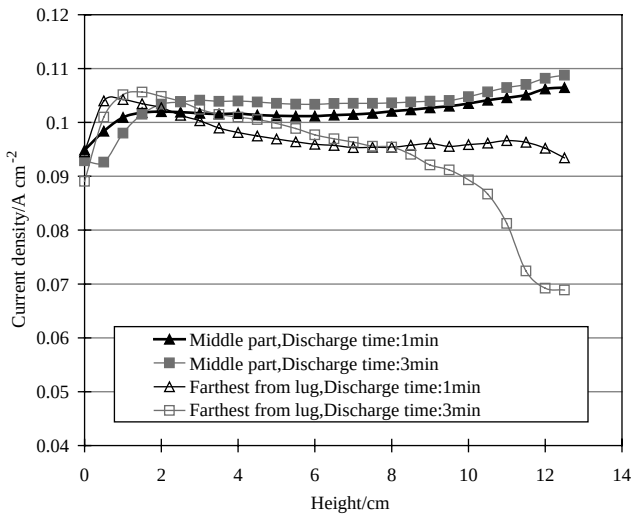

Fig. 13. Distribution of current density in the middle of the negative plate and farthest from the lug. Discharge current: 36 A. Temperature: −18 °C.

distribution of current density in the middle part of the plate and at the points farthest from the lug at discharge times of 1 and 3 min at −18 °C. The current density hardly increases in the middle part of but at the end of discharge the current density at the points farthest from the lug and at the top of the plate falls greatly, while it increases in the middle.

4. Conclusions

During discharge of an automotive battery negative plate, the distributions of its current density and potential were obtained by measuring the *IR* drop in the H_2SO_4 solution between the positive and negative plates. At the end of discharge, high polarization appears at the top and bottom of the plate and the current density falls very quickly in these regions. When a negative plate is discharged, the polarization resistance is defined by the ratio of the polarization potential to the current density. The resistance of the active mass increases very quickly at the top and bottom during discharge and causes the capacity of the negative plate to decrease and the cycle life shorten. The resistance of the active mass is mainly caused by passivation of the negative plate and it decreases under constant current charge. It is essential to change charge conditions so as to ensure complete charge of the plate and to reduce the resistance of the negative plate.

When the negative plate is discharged at low temperature, the polarization in the middle of the plate changes little. However, the highest polarization appears farthest away from the lug and at the top of the plate and the current density drops sharply at the end of discharge in these regions.

Acknowledgements

The authors are grateful to NSFC (No. 20373037) in China for financial support for this work and thank Dr. Pamela Holt, Shandong University, for helpful suggestions on the manuscript.

References

1. K. Asai, T. Hatanaka, M. Tsubota and K. Yonezu, *J. Power Sources* **16** (1985) 65.
2. W.G. Sunu and B.W. Burrows, *J. Electrochem. Soc.* **128** (1981) 1405.
3. M. Calábek, K. Micka, P. Baca and P. Křivák, *J. Power Sources* **85** (2000) 145.
4. P. Král, P. Křivák, P. Bača, M. Calábek and K. Micka, *J. Power Sources* **105** (2002) 35.
5. Y. Guo, W. Li and L. Zhao, *J. Power Sources* **116** (2003) 193.
6. Y. Guo, Y. Li, G. Zhang, H. Zhang and J. Garche, *J. Power Sources* **124** (2003) 271.
7. W.H. Tiedemann, J. Newman and F. Desua, *J. Power Sources* **6** (1977) 15.
8. W.G. Sunu and B.W. Burrows, *J. Electrochem. Soc.* **129** (1982) 688.
9. W.G. Sunu and B.W. Burrows, *J. Electrochem. Soc.* **131** (1984) 1.
10. L.E. Vaaler and E.W. Brooman, *J. Appl. Electrochem.* **12** (1982) 721.
11. J. Landfors and D. Simonsson, *J. Appl. Electrochem.* **25** (1995) 315.
12. Y. Guo, M. Wu and S. Hua, *J. Power Sources* **64** (1997) 65.
13. G. Petkova and D. Pavlov, *J. Power Sources* **113** (2003) 355.