Studies of the current and potential distributions on lead-acid batteries III. Formation of the single-side pasted automotive positive plate

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Abstract

The formation processes of the single-side pasted automotive positive plate have been studied by an in situ electrochemical scan technique. On the pasted side of the positive plate, its polarization is very high and its charge current is very low at the beginning of the formation, compared with those on the non-pasted side. Then, their difference becomes smaller and smaller with the formation. Moreover, the distributions of the current density and the polarization resistance are quite uneven on the pasted side at the initial stage of the formation. The lowest current density and the highest polarization resistance are located in the middle. At the later stage, the charge current on the pasted side becomes a little higher, but its charge amount is still lower than that on the non-pasted side. Although the conductivity of PbO_2 zones is very good, the violent charge at the high polarization will lead to the increase of the contact resistance between the active mass particles at the beginning of the formation.
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1. Introduction

The formation of the lead-acid battery plates is one of the important processes in their production. The tank and container formation is often used in the manufacture of lead-acid batteries [1–2]. Most automotive lead-acid batteries are produced by the tank formation, while many valve-regulated lead-acid (VRLA) batteries, especially large batteries are produced by the container formation. In any event, the formation of the positive plate is more difficult than that of the negative plate [3]. This is mainly due to the change of volume from the paste to the active mass. In the formation, the lead monoxide and the basic lead sulfates are transformed into the lead dioxide on the positive plate, which makes the porosity in the active mass decrease and the ion diffusion more difficult. On the negative plate, it is the sponge lead that is formed. Its volume shrinkage improves the ion diffusion in the formation. Therefore, many investigations have been concentrated on the formation of the positive plate [4–8].

The optimal composition and structure of the active mass formed in the plate manufacture are quite important to the initial capacity and the battery life [9–11]. The factors influencing tank formation include the formation time, the charge current profile, the charge amount, the electrolyte temperature and its specific gravity [3,12–14]. For the formation of the positive plate, the key is the content of the total PbO_2 and the ratio of α- to β-PbO_2, which determines the structure of the active mass. The formation time usually depends on the production period of the factory. The specific gravity of sulfuric acid significantly influences the charge efficiency and the ratio of α- to β-PbO_2 in the active mass of the positive plate [8]. The high sulfuric acid concentration can promote the formation of β-PbO_2. The electrolyte of 1.03–1.10 g cm^{-3} is often used for the positive plates with different thickness. Elevating electrolyte temperature can increase the content of PbO_2, but it is normally less than 50 °C. The temperature is adjusted by the electrolyte amount and the charge current profile. The latter is very important for the composition and performance of the positive plate [15]. In practice, almost all positive plates are evaluated by the PbO_2 content and the initial capacity of the battery. However, the effects of the formation on the battery life are, in most cases, estimated on the basis of the experience. Few investigations have been done in this aspect.

It is well known that the shedding of the active mass on the positive plate is one of the main factors, which limits the battery

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life [16–19]. It is closely related to the internal stress produced in the violent gassing during overcharging. In the later stage of the formation, especially at high temperature, the high charge current also leads to the shedding of the active mass on the positive plate. The optimal formation is to get the high PbO_2 content and to prevent overcharging. However, in reality, it is difficult to form the positive plate uniformly because of the grid design and its manufacture, especially when most paste machines are only single-side pasting ones. Therefore, the local overcharge is inevitable on the positive plate of automotive lead-acid batteries.

In our previous work, an in situ electrochemical scan technique has been established to determine the current and potential distributions of the positive plates [20–22]. In this paper, this technique is used to study the formation process of the single-side pasted positive plate of automotive lead-acid batteries, in order to improve the performances of the positive plate.

2. Experimental

The test positive and negative plates were produced by the single-side pasting machine in the factory. The grids used were cast by Pb–Ca–Sn alloy and were the radiation design with the dimensions of 14.3 cm (W) × 11.2 cm (H) × 0.16 cm (T). The pasted positive plate was 0.18 cm thick and had about 86 g dry paste. So, there is a 0.02 cm-thick layer of active mass over the grid (pasted side). Its C_{20} capacity was 11 Ah. The formed plates were applied to the automotive lead-acid batteries. Fig. 1 shows the positive plate photographs of the pasted and non-pasted sides. The profile of the radiation grid ribs is visible in Fig. 1B.

In the formation, the test positive plate was put in between two negative plates. The container used had the internal dimensions of 14.5 cm (W) × 9 cm (L) × 15 cm (H). The distance between the positive and negative plates was about 4.2 cm (for measuring the current density, not for practical formation). This allowed three couples of reference electrodes to be placed between the plates, to measure the IR voltage drop in the electrolyte and the potential of the positive plate. Each side of the positive plate was divided into six channels and 138 parts. The current density of each part was calculated via the measured voltage drop in the electrolyte. The measurements of the in situ electrochemical

scan were similar to those in ref. [21]. One scan could measure three channels by moving three couples of the reference electrodes from bottom to top of the plate. At different formation times, the current and potential distributions on both sides of the positive plate were obtained every four scans. The potential reported in this paper was against the $Hg/Hg_2SO_4/H_2SO_4$ (1.285 g cm^{-3}) reference electrode. The data were recorded by a HP 34970 A Data Acquisition/Switch Unit connected to a PC.

In the formation, the electrolyte of 1.05 g cm^{-3} H_2SO_4 was used. The soaking time was about 1 h before the charge. After that, the positive plate was formed at 2.1 A for 10 h, and then the charge current was changed into 1.05 A and lasted for 12 h. The electrolyte temperature was between 41 and 45 °C.

3. Results and discussion

3.1. Distributions of current density

In order to compare the difference on the two sides of the single-side pasted positive plate, their current and potential distributions have been measured in the formation. In the experiment, the width of the formation container and the height of the H_2SO_4 electrolyte were the same as the dimensions of the test positive plate, to ensure the ion flowing between positive and negative plates, which was parallel to each other. So, the measured IR voltage drop in the electrolyte was proportional to the local current density on the positive plate. When three couples of reference electrodes measuring IR drop were moved from the bottom to top of the plate twice, six channels and 138 points were measured on one side of the positive plate. Four scans could obtain the data of the IR drop and the potential with 276 points on both sides. It means that total charge current of the positive plate is proportional to the sum of 276 IR drops. Therefore, the local current density, i, is expressed by:

$$i = \frac{\Delta U \times I}{1.16 \times \sum \Delta U} \tag{1}$$

where ΔU denotes the IR voltage drop measured in the electrolyte, $\sum \Delta U$ the sum of 276 IR voltage drops on both sides of the positive plate and I is the charge current in the for-
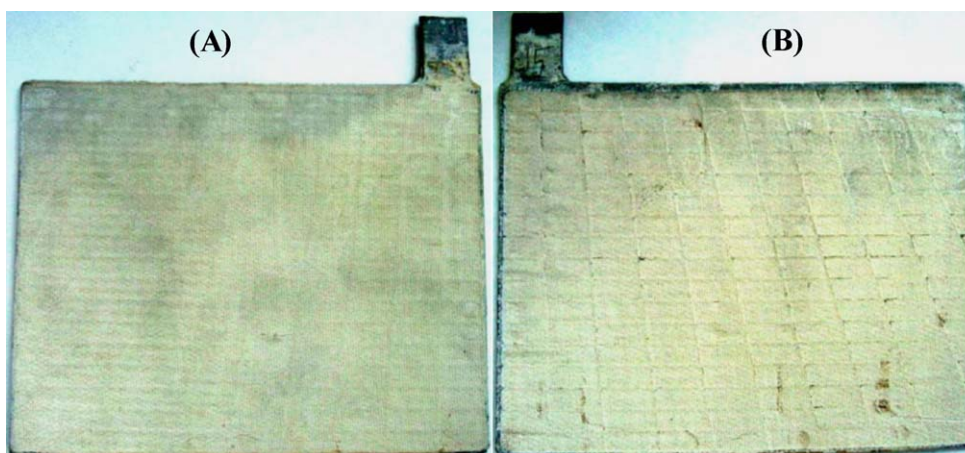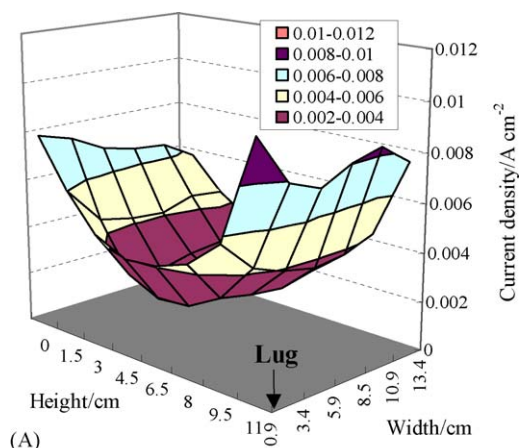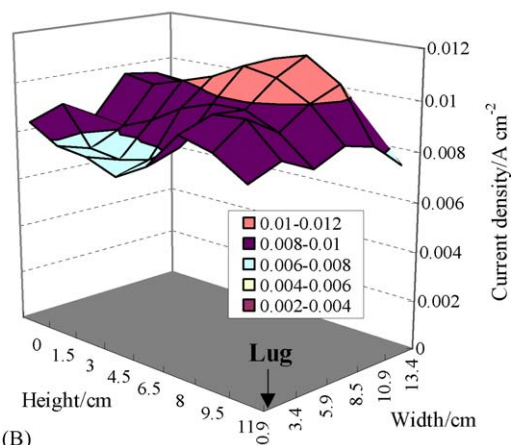

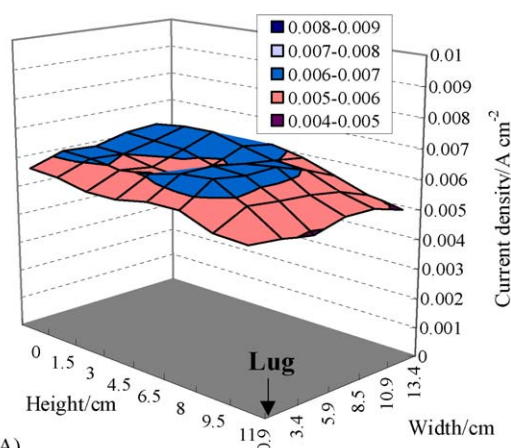Fig. 1. Photographs of the pasted automotive positive plate. (A) Pasted side and (B) non-pasted side.
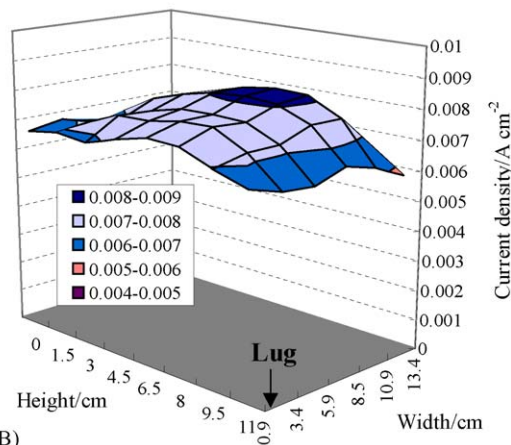
Fig. 2. The distributions of the current density on the positive plate. Formation time: 5 min and charge current: 2.1 A. (A) Pasted side and (B) non-pasted side.

Fig. 3. The distributions of the current density on the positive plate. Formation time: 2 h and charge current: 2.1 A. (A) Pasted side and (B) non-pasted side.

mation, which is 2.1 A within 10 h, and then is changed into 1.05 A.

Figs. 2–4 show the current density distributions on both sides of the automotive positive plate at different formation times. Fig. 2 shows that at the beginning of the formation, the current density distributions on both sides of the positive plate are quite different. The current density on the pasted side is much lower and their average current density is 4.4 and 9.1 mA cm^{-2}, respectively. On the pasted side in Fig. 2A, the current density distribution is quite uneven. And the current density around the plate is much higher than that in the middle. It is obvious that this is related to the good conductivity of the grid frame. Since the paste is a very poor conductor, there is an extra high-resistance layer and an extra voltage drop over the grid. So, the paste on the pasted side has a low electrochemical polarization, which results in low current density. On the non-pasted side, the high current density appears in Fig. 2B because this side does not have the cover layer of paste and has good conductivity. As the conductive zones of PbO$_2$ are formed in the formation, the current density on the pasted side becomes higher and higher, while it decreases on the non-pasted side because of the unchanged charge current. But Fig. 3 shows that the current density on the pasted side is still lower than that on the non-pasted side after 2 h formation. Their average current density is 5.8 and 7.2 mA cm^{-2}, respec-

tively. In comparison with Fig. 2, the current density distribution becomes more uniform in Fig. 3. With the formation, the difference on the two sides of the positive plate becomes increasingly small. After 5 h formation, the average current density is 6.5 and 6.4 mA cm^{-2} on the pasted and non-pasted sides, respectively. So, at this time, the charge current on both sides is very symmetrical. But the charge amount on the non-pasted side is more than that on the pasted side. Therefore, the average current density increases continuously on the pasted side while it decreases slowly on the non-pasted side. At 10 h, it is 6.8 and 6.2 mA cm^{-2}, respectively. After that, the charge current is reduced to a half. Fig. 4 shows the current density distributions on both sides at the end of the formation. The average current density is 3.4 and 3.1 mA cm^{-2}, respectively. And it is found that the current density distribution on the pasted side is more uneven. The low current density is located around the plate while the maximum appears in the middle. This may be related to the violent charge at a high polarization near the grid frame at the beginning of the formation.

To further understand the change of the current density distributions, Fig. 5 shows the current density distributions on both sides in the middle of the positive plate in the formation. Great changes take place in the current density. On the pasted side, the high current density appears at the bottom and top of the plate
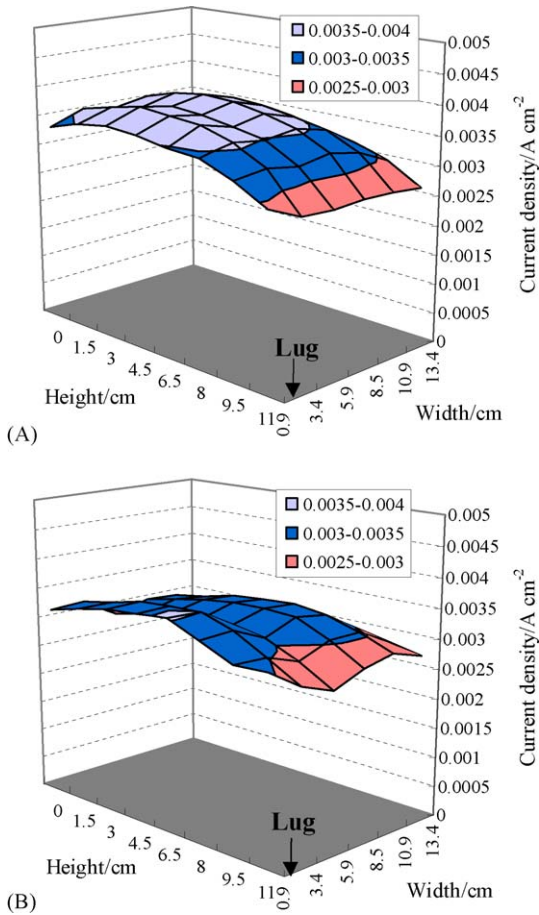
Fig. 4. The distributions of the current density on the positive plate. Formation time: 22 h and charge current: 1.05 A. (A) Pasted side and (B) non-pasted side.
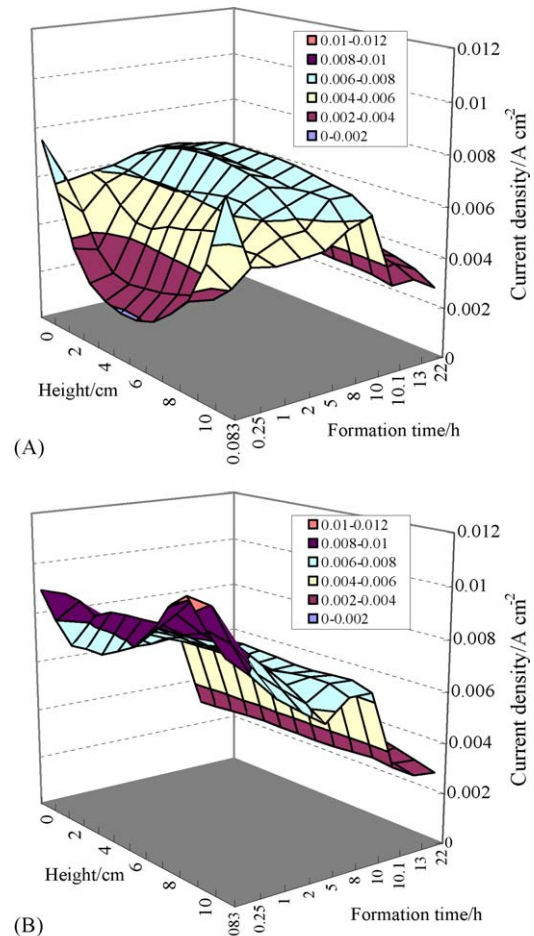

Fig. 5. The evolution of the current density distributions in the middle of the positive plate in the formation. Charge current: 2.1 A from 0 to 10 h and 1.05 A from 10 to 22 h. (A) Pasted side; (B) non-pasted side.

at the beginning of the formation, but later it drops quickly. However, the current density increases gradually in the middle. During the 5–10 h period, it changes a little. On the non-pasted side, the current density is relatively uniform up and down the plate, but it decreases continuously within 5 h. After 10 h, the current density distributions are very uniform on both sides of the positive plate.

3.2. Potential distributions

In the two scans of the reference electrodes on each side, we can obtain 138 data of the potential from the reference electrodes close to the surface of the positive plate. Since there is about 4.5 mm gap between its surface and the Luggin capillary tip of the reference electrode, the potential of the positive plate above has been corrected by the *IR* voltage drop measured in the electrolyte. Figs. 6 and 7 show the potential distributions on both sides of the automotive positive plate at the beginning and end of the formation. It is found that the potential distributions in Fig. 6 are relatively uniform, compared with the current density distributions in Fig. 2, especially on the pasted side. But the positive electrode potential is very high at the beginning of the formation. The potential on the pasted side is also much higher than that on the non-pasted side and their average potentials are 1.361 and 1.246 V, respectively. It is clear that the extra polar-

ization of 115 mV is caused by the pasted layer over the grid. In addition, some potential difference exists between the middle and edge of the plate. Around the plate, the potential is lower on the pasted side while it is higher on the non-pasted side. As the positive plate is formed, the potential drops more quickly in the middle of the pasted side. During the 2–5 h period, the potential in the middle of both sides is lower than that around the plate and their difference is about 15–20 mV. This can be explained from two aspects. On one hand, the potential of the positive plate is mainly determined by the paste conductivity in the formation. On the other hand, it is also related to the resistance of the grid/active mass interface as well as to the contact resistance between the active mass particles. On the pasted side, the pasted layer over the grid has a very high resistance. So, the formation at first begins near the grid frame because of its good conductivity. As the paste is formed, the paste conductivity increases quickly and the polarization drops rapidly. During the 2–5 h period, the paste conductivity is so high that its polarization is not dominant. Instead the contact resistance between the active mass particles becomes dominant. And the violent charge at very high potential can also easily lead to high contact resistance between active mass particles around the plate at the beginning of the formation. Therefore, the high
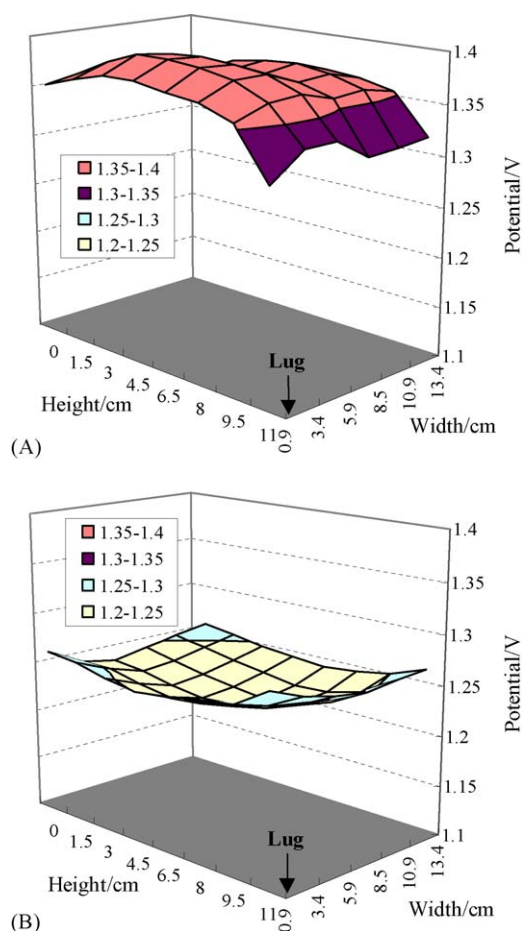
Fig. 6. The potential distributions of the positive plate. Formation time: 5 min and charge current: 2.1 A. (A) Pasted side and (B) non-pasted side.
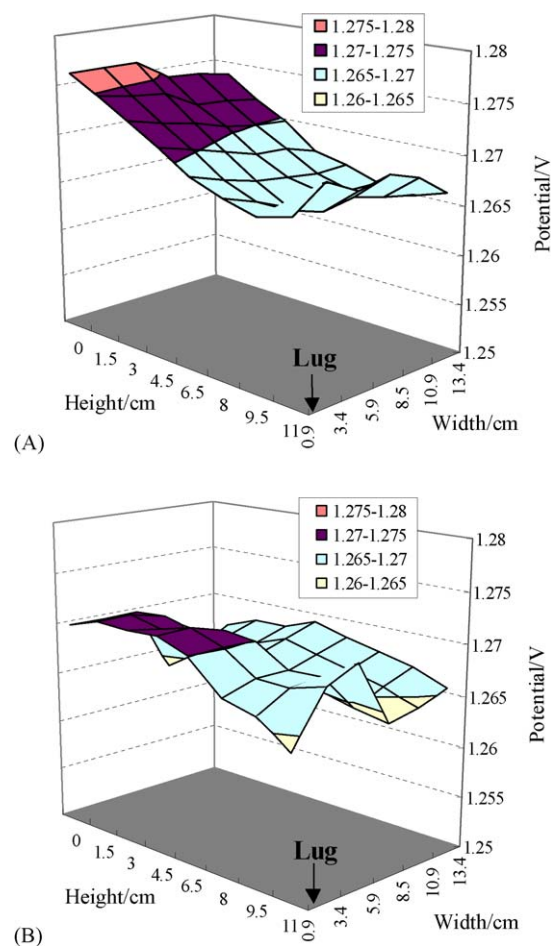

Fig. 7. The potential distributions of the positive plate. Formation time: 22 h and charge current: 1.05 A. (A) Pasted side and (B) non-pasted side.

polarization will appear around the plate of both sides after the formation.

Fig. 7 shows that at the end of the formation, the potential distributions are relatively uniform. Their average potentials are the same on both sides of the plate and equal to 1.270 V. But there still exits some uneven distributions of the potential on the pasted side. Fig. 7A shows that the potential difference is about 10 mV up and down the plate. It means that the lower part on the pasted side has a high polarization, which will become more serious for the large battery.

To know the evolution of the potential, Fig. 8 shows the distributions of the average potential on both sides of the positive plate at different formation times. It can also be seen from Fig. 8 that the average potential on the pasted side is much higher than that on the non-pasted side within 2 h. And their difference becomes smaller and smaller. During the 2–5 h period, the potential reaches the minimum. After that, it increases gradually. At 10 h, the potential drops due to the change of the charge current. According to our previous work [22], it is believed from the change of the potential that the formation rate is controlled by the paste conductivity during the first 2 h formation while the electrochemical reactions become dominant after the 5 h formation. During the 2–5 h period, both the paste conductivity and the electrochemical reactions affect the formation rate.

3.3. Distributions of polarization resistance

Since the paste conductivity is very poor, great changes take place in the polarization resistance of the positive plate in the formation. To obtain the polarization resistance distributions on both sides of the plate, we define the local polarization resistance
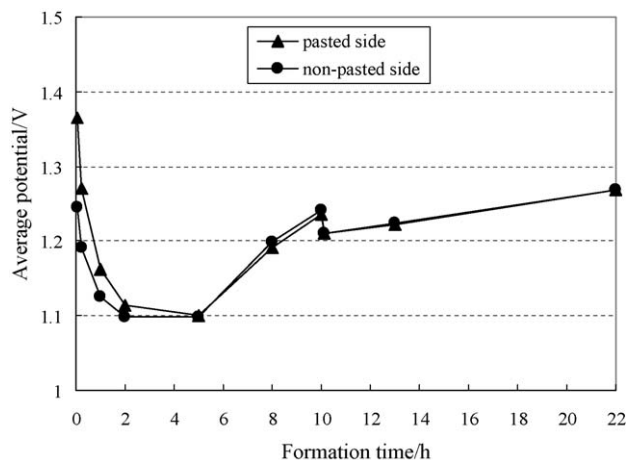

Fig. 8. The evolution of the average potential on both sides of the positive plate in its formation.
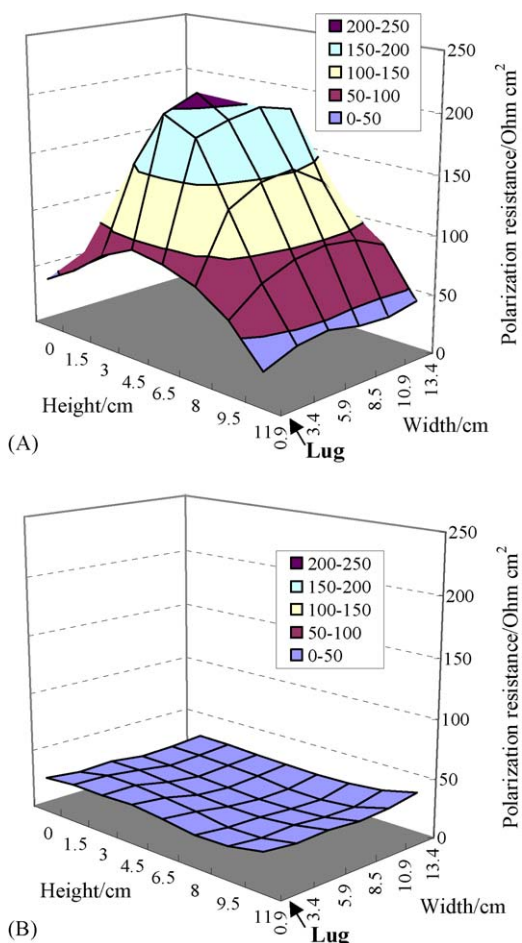
Fig. 9. The distributions of the polarization resistance on the positive plate. Formation time: 5 min and charge current: 2.1 A. (A) Pasted side and (B) non-pasted side.
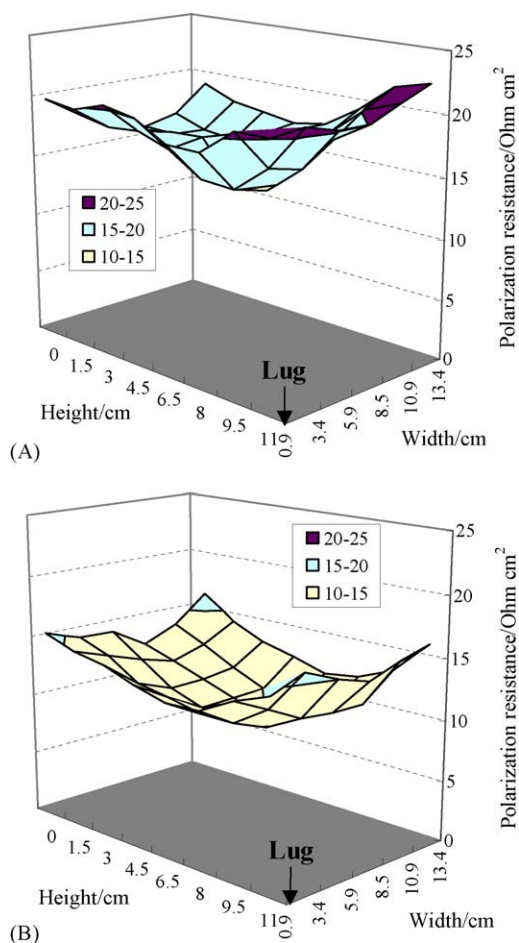

Fig. 10. The distributions of the polarization resistance on the positive plate. Formation time: 2 h and charge current: 2.1 A. (A) Pasted side and (B) non-pasted side.

per unit area as the ratio of the polarization to the local current density. The polarization of the positive plate is the difference between the measured electrode potential and the potential at open circuit, which is 1.01 V after the formation. On the basis of the measured data of the current density and the potential, the distributions of the polarization resistance can be calculated. Figs. 9–11 show the distributions of the polarization resistance on both sides of the positive plate at different formation times. It is found from Fig. 9 that the polarization resistance is very high and its distribution is also quite uneven on the pasted side. And the maximum polarization resistance appears in the middle and reaches 211 $\Omega\,cm^2$. The low polarization resistance around the plate is due to the good conductivity of the grid frame. On the contrary, the polarization resistance is very small and its distribution is uniform on the non-pasted side. The average polarization resistance is 112 and 26 $\Omega\,cm^2$ on the pasted and non-pasted sides, respectively. As the PbO_2 zones are formed in the formation, the polarization resistance drops quickly, especially on the pasted side. Fig. 10 shows that the polarization resistance is very low and its distributions are relatively uniform on both sides at 2 h formation. The average polarization resistance is 17 and 12 $\Omega\,cm^2$ on the pasted and non-pasted sides, respectively. And the greatest difference of the polarization resistance on each

side is less than 7 $\Omega\,cm^2$. It is also found that the polarization resistance around the plate is higher than that in the middle. This is related to the violent charge at a high polarization at the beginning of the formation. In the later stage of the formation, the polarization resistance increases again. Fig. 11 shows that the distributions of the polarization resistance on both sides of the positive plate at the end of the formation. Although the distributions are relatively uniform on both sides, their polarization resistance becomes very high. The average polarization resistance is 76 and 83 $\Omega\,cm^2$ on the pasted and non-pasted side, respectively. And on the former, the polarization resistance in the upper part is higher than that in the lower part. Since the conductivity of the PbO_2 zones is very good, the high polarization resistance is caused by the electrochemical reactions rather than the ohmic resistance in the later stage of the formation.

To know the evolution of the polarization resistance, Fig. 12 shows the change of the average polarization resistance on both sides of the positive plate during the formation. It is found that the average polarization resistance drops quickly during the first 2 h formation and it keeps the minimum in the period of 2–5 h, and then increases gradually. At the former stage of the formation, the average polarization resistance on the pasted side is much higher than that on the non-pasted side. This is because
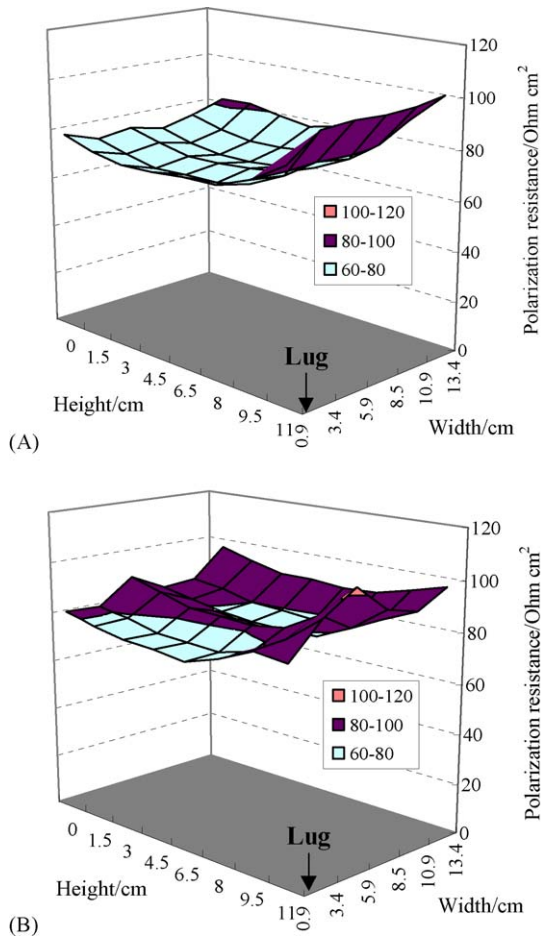
Fig. 11. The distributions of the polarization resistance on the positive plate. Formation time: 22 h and charge current: 1.05 A. (A) Pasted side and (B) non-pasted side.

there is an extra-pasted layer on the pasted side. But, in the later stage, the average polarization resistance on the pasted side is lower than that on the non-pasted side. It is clear at this time that the thickness of the active mass of this layer is not dominant for the polarization resistance. Instead the contact resistance
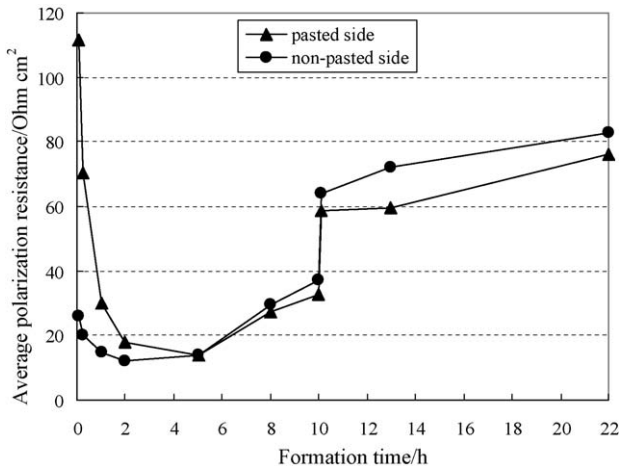
between the active mass particles becomes dominant. At the later stage of the formation, the higher polarization resistance on the non-pasted side is due to the violent charge in these regions at the beginning of the formation, which leads to the poor contact between the active mass particles.

3.4. Distributions of charge amount

Since great changes take place in the current density on both sides of the positive plate, it is significant to know the charge amount of each side in the formation. We have measured the current density and potential distributions 10 times at different formation times. On the basis of the local current density and the measuring interval, the local charge amount can be calculated in the formation. Fig. 13 shows the distributions of the charge amount on both sides. It is found that their distributions are relatively uniform. Although the grid frame has a good conductivity, the low charge amount appears near the frame, especially on the top in Fig. 13A, rather than in the middle. And the charge amount on the pasted side is a little lower than that on the non-pasted side. They are 16.41 and 16.65 Ah, respectively. Fig. 14 shows the evolution of the charge current and the charge amount on both sides of the positive plate in the formation. The charge current on both sides is quite different. At the beginning of the

Fig. 12. The evolution of the average polarization resistance on both sides of the positive plate in its formation.
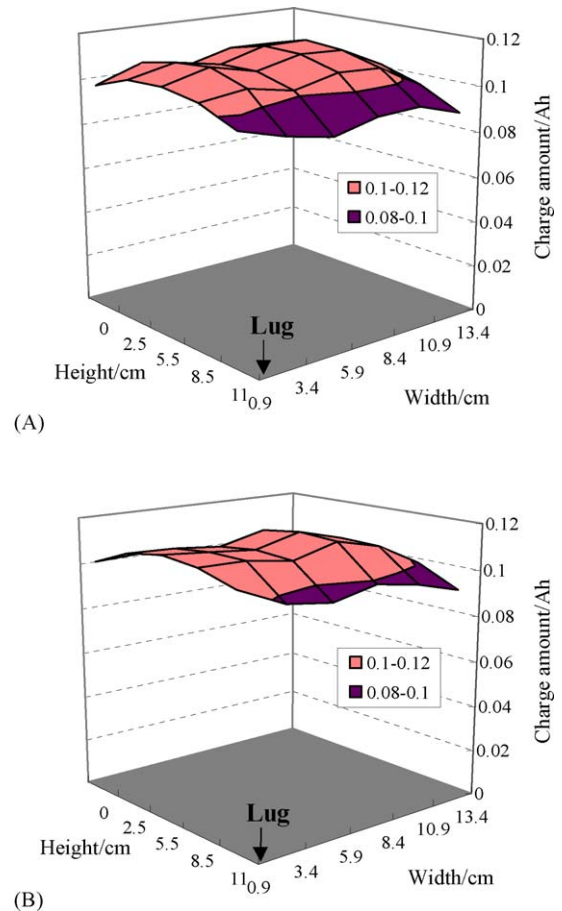

Fig. 13. The distributions of the charge amount on both sides of the positive plate. (A) Pasted side and (B) non-pasted side.
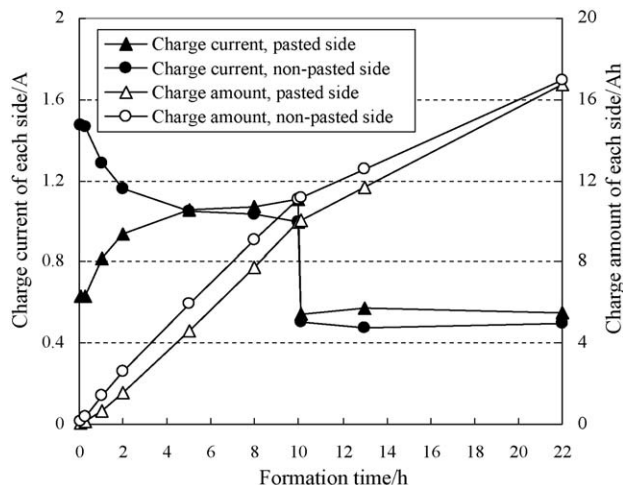
Fig. 14. The evolution of the charge current and charge amount on both sides of the positive plate in its formation.

formation, the charge current on the non-pasted side is much higher. Then, the charge current drops gradually on the non-pasted side while it increases on the pasted side. After 8 h, the charge current on the pasted side becomes higher. Yet, even if it is so, the charge amount on the pasted side is always lower than that on the non-pasted side. It means that the initial charge current is very important to the charge amount of each side in the formation.

4. Conclusions

In the formation of the single-side pasted automotive positive plate, great changes take place in the current density distributions on both sides. At first, the formation begins from all parts of the entire plate on the non-pasted side and from the grid frame on the pasted side. So, the current density is very low in the middle of the pasted side. Then, with the formation, the current density increases on the pasted side while it decreases on the non-pasted side. It lasts for about 5 h. At this time, the charge currents on both sides become almost the same. After that, the charge current on the pasted side becomes a little higher than that on the non-pasted side. At the end of the formation, however, the charge amount is still lower on the pasted side. Although the conductivity of the grid frame is good, the charge amount is low in these regions, especially on the top of the plate. The maximum charge amount is in the middle where the charge current density is very low on the pasted side at the beginning of the formation.

During the first 2 h formation, the positive electrode potential drops quickly. It reaches the minimum and is almost stable in the period of 2–5 h. Then, it increases continuously. Since the paste is a very poor conductor, the polarization on the pasted side is much higher than that on the non-pasted side at the beginning

of the formation. However, the difference becomes smaller and smaller with the formation. After 5 h, the potentials on both sides are almost the same.

At the beginning of the formation, the polarization resistance on the pasted side is much higher than that on the non-pasted side. And on the pasted side, its maximum is in the middle while very low polarization resistance appears around the plate because of the good conductivity of the grid frame and the low polarization in these regions. As the formation is performed, the polarization resistance drops rapidly and reaches a very small value during the 2–5 h period. Then, it increases continuously.

In the formation, the polarization resistance depends not only on the paste conductivity and the charge transfer but also on the contact resistance between the active mass particles as well as the grid/active mass interface, etc. The violent charge at the beginning of the formation and the overcharge in the later stage will lead to the increase of the contact resistance. Therefore, for the formed positive plate, the polarization resistance on the non-pasted side is higher than that on the pasted side.

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