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# Changes in the structure of active materials in lead–acid batteries

Q. Dengke *

*Guangzhou Storage Battery Enterprises, 1-1 Huayuan Road, Sanyuanli, Guangzhou, China*

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**Abstract**

A study has been made of the effect of leady oxide with different characteristics (density, particle size, surface area) on the structure and properties of positive and negative plates of lead–acid batteries. 

*Keywords:* Density; Lead–acid battery; Oxide; Particle size; Plate surface area

## 1. Introduction

An important part of our research programme on lead–acid batteries is to study the characteristics of continuous changes in the active materials of the plates [1,2]. Compared with 'memory effects' [3,4], fewer experimental data have been reported for these changes. Nevertheless, results to date show that such features do exist in the conversion processes of the active materials.

## 2. Experimental

All materials, except those used in investigations of the structure of the porous mass, were well-dispersed in inert media by ultrasonic vibration.

Two types of milled lead oxide—oxide A and oxide B—were used. These oxides have similar levels of oxidation, but differ in structure and particle size. The particle shape, effective density, particle size (including distribution) and BET surface area were analyzed (see Table 1).

Using the same production process, plates were made from either the series A or the series B oxide. The characteristics of these plates were compared.

## 3. Results and discussion

### 3.1. Continuous changes in shape

The main features of the continuous change in oxide structure are listed in Table 2. Scanning electron micrographs reveal (Fig. 1) that irregular, more compact particles develop in the series A plates during conversion of oxide to positive and negative active materials. In series B plates, however, regular continuous changes take place in the larger, looser particles (Fig. 2).

### 3.2. Continuous changes in effective particle density

The data presented in Table 3 shows that the smaller, tightly packed, oxide A has a large effective density. This feature is maintained in both plate types before formation. After formation, the effective densities of series A and series B are much closer in value.

The continuous changes do not exhibit the consistency which exists in the 'memory effect'. Moreover, the nature of the changes is not maintained during the conversion of oxide to active materials.

Table 1
Techniques used to determine lead oxide properties

| Test programme | Investigative instrument |
|---|---|
| Structure (SEM) | JCXA-733 (Japan) |
| Effective density | Pycnometer method |
| Particle size and distribution | SHUMADZU-SA-CP3 (Japan) |
| BET surface area | COULTER-SA3100 (USA) |

* Tel.: +86-20-8655-9900; Fax: +86-20-8656-4910; E-mail: qdengke@public1.guangzhou.gd.cn

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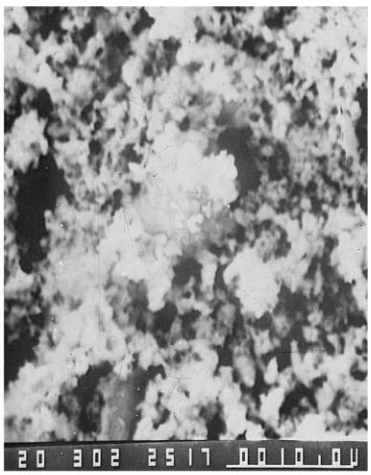
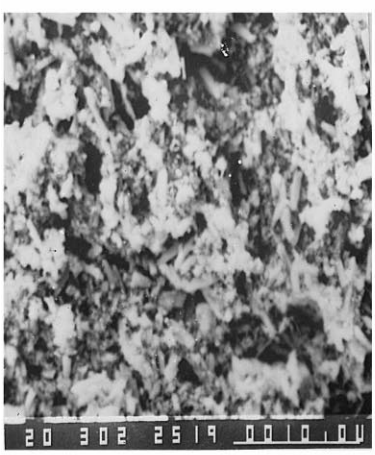
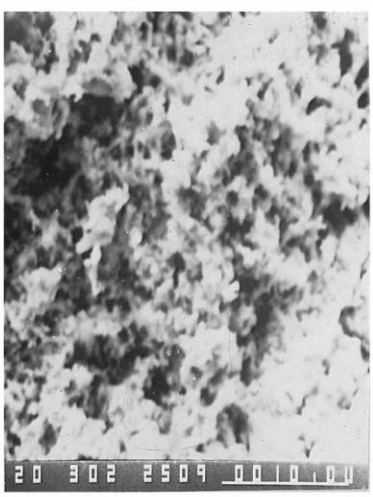




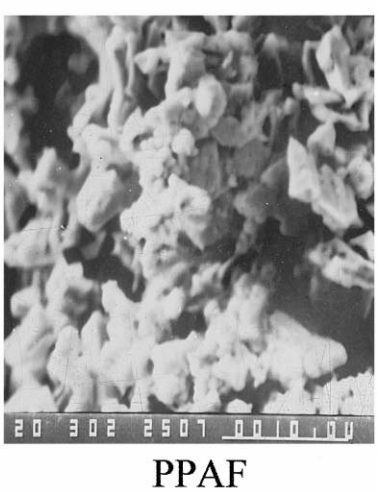
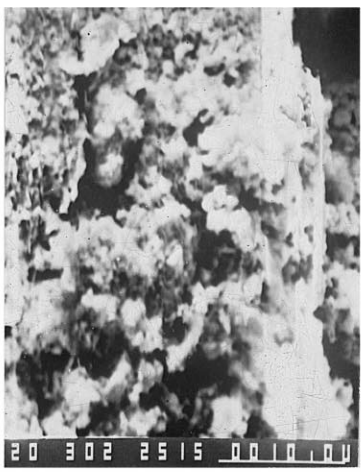
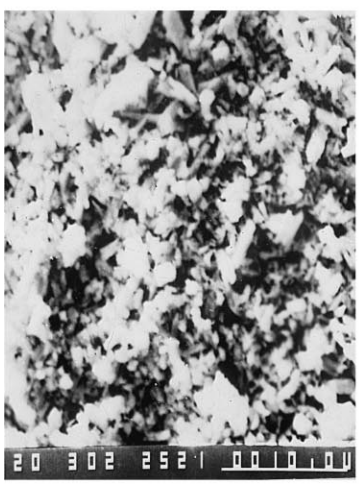



Fig. 1. Electron micrographs of series A oxide and negative (NPBF, NPAF) and positive (PPBF, PPAF) active material before and after plate formation (×3000).



OXIDE



NPBF

NPAF

PPBF

PPAF

Fig. 2. Electron micrographs of series B oxide and negative (NPBF, NPAF) as well positive (PPBF, PPAF) active material before and after plate formation (×3000).

### 3.3. Continuous changes in particle median diameter and particle-size distribution

The median diameter of series A particles is smaller than that of series B particles (Table 4). The ratio (0.86 + 0.01) of the oxide median diameter of series A and series B particles is very close to that in the plate after formation. This finding holds for both plate polarities.

The particle-size distribution of series A and series B oxide is shown in Figs. 3 and 4, respectively. Series A

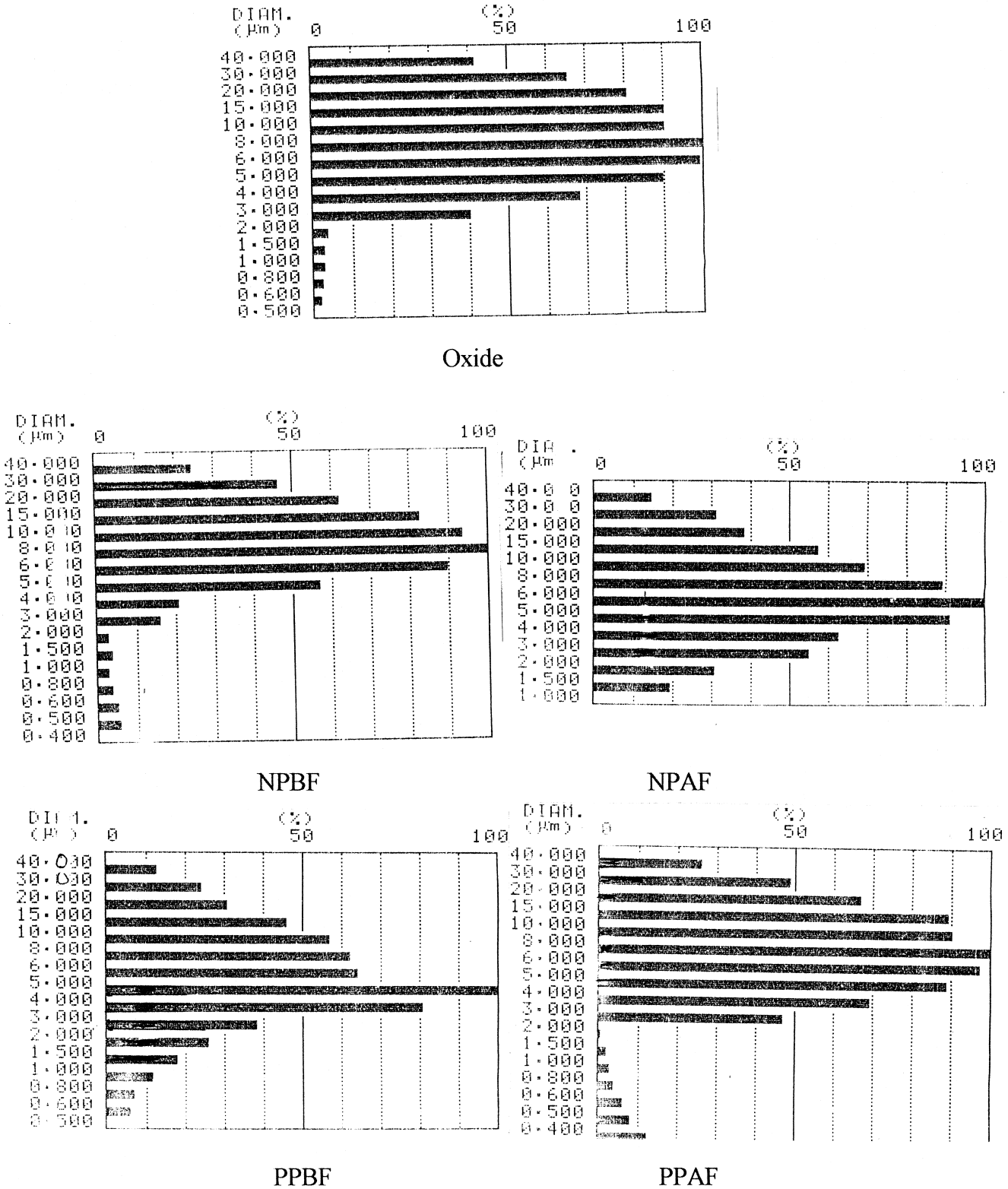



Fig. 3. Particle-size distribution of series A materials.

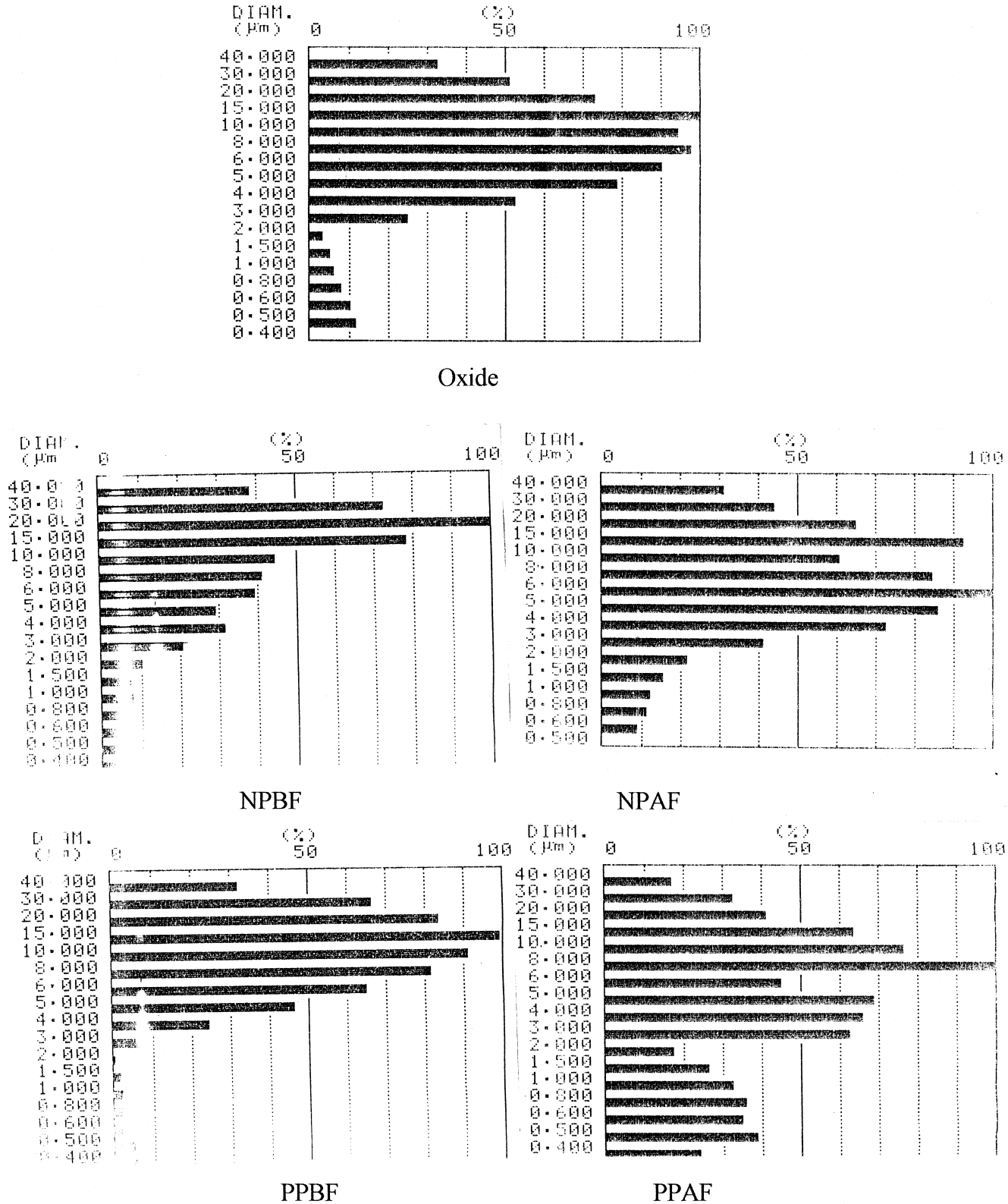



Fig. 4. Particle-size distribution of series B materials.

plates display an excellent normal distribution of particle size. By contrast, the distribution of series B is more dispersed. The continuity of the particle-size distribution is more obvious than that of the median diameter.

## 4. Continuous changes of BET surface area

The data in Table 5 show that the ratio of the BET surface area of the oxide in plates A and B is similar to

Table 2
Continuous changes in oxide structure

| Features | Series A plate | Series B plate |
|---|---|---|
| Oxide | small and irregular particles, packed closely together | 'fish scale' and larger particles, packed loosely together |
| NPBF | regular, compact | cubic form, loose |
| NPAF | connected structure | disconnected coralloid structure |
| PPBF | irregular, compact | cubic form, loose |
| PPAF | irregular, compact | cubic form, loose |

NPBF = active material of negative plate before formation; NPAF = active material of negative plate after formation; PPBF = active material of positive plate before formation; PPAF = active material of positive plate after formation.

Table 3
Effective particle density ($D$) of active materials

| $D$ (g cm$^{-3}$) | Oxide | NPBF | NPAF | PPBF | PPAF |
|---|---|---|---|---|---|
| Series A | 10.32 | 8.36 | 9.96 | 8.06 | 8.90 |
| Series B | 9.37 | 7.69 | 10.08 | 7.71 | 9.04 |

Table 4
Median particle diameter

| Median diameter | Oxide | NPBF | NPAF | PPBF | PPAF |
|---|---|---|---|---|---|
| Series A | 7.21 | 2.15 | 5.72 | 4.89 | 3.67 |
| Series B | 8.31 | 11.37 | 6.69 | 10.78 | 4.31 |
| A:B | 0.87 | | 0.86 | | 0.85 |

Table 5
BET surface area

| BET (m$^2$ g$^{-1}$) | Oxide | NPBF | NPAF | PPBF | PPAF |
|---|---|---|---|---|---|
| Series A | 0.937 | 1.53 | 0.907 | 0.990 | 2.40 |
| Series B | 0.800 | 1.35 | 0.705 | 0.860 | 1.85 |
| A:B | 1.17 | 1.13 | 1.29 | 1.15 | 1.30 |

that in NPBF and PPBF samples (viz., 1.13–1.17). The ratio becomes larger after formation, and has virtually the same value in negative and positive plates (viz., 1.29 vs. 1.30).

## 5. Conclusions

Continuous changes in the crystalline form of plate active material have been widely studied as a 'memory effect' [3,4]. By contrast, changes in the shape, size distribution, and BET surface area have received less attention. These latter changes are thought to be less systematic [5,6]. As matter of fact, research on continuous changes is of direct importance to the manufacturing of lead–acid batteries.

There are continuous changes in the features of the conversion of oxide to the active materials of the plates; these features include: shape, effective density, particle-size distribution, and BET surface area. By analyzing oxide characteristics, it is possible to predict some of these features, both before and after formation. Favourable features can be retained while detrimental ones can be ameliorated through improvement in the design of the manufacturing process. For example, the surface area of active materials must be different for high current discharge and low current deep discharge. Oxides with different surface area can be used to make different plates, or the quantity of acid can be changed to adjust the surface area of the active materials.

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