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Short communication

Increase of positive active material utilization in lead-acid batteries using diatomaceous earth additives

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Abstract

In this study we examined the use of diatomites to improve the discharge capacity and utilization of the positive electrode of the lead-acid battery. A large fraction of the positive electrode performance of this battery system (half-reaction shown below) is based on the ionic conduction of sulfuric acid through the plate.

$$\mathrm{PbO_2(s) + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O}$$

The porous diatomites improve the ionic conduction by providing channels in addition to the natural ones formed within the paste. The choice of diatomite is based on its stability in the oxidative and corrosive environment of the lead-acid battery, as well as its naturally high porosity. The diatomite particles were size sorted into 20–30 μm, 30–53 μm, 53–74 μm, and 74–90 μm fractions, and the discharge performances of each were measured at 1%, 3%, and 5% weight ratios. The best performance was observed with 53–74 μm particles with an optimum weight ratio of 3%. At this size fraction and weight ratio, diatomites show a 12.7% increase in active material utilization and a 9.3% increase in specific capacity at high rate discharge (50 mA cm^{-2}) relative to control samples without diatomites.

Keywords: Active material utilization; Specific capacity; Porous additive; Lead-acid battery; Positive electrode

1. Introduction

The lead-acid battery is a highly successful rechargeable electrochemical storage system. Despite its design dating from Plante in 1859, the system can benefit from new approaches.

During discharge, lead (Pb) negative and lead dioxide (PbO_2) positive plates are converted into lead sulfate ($PbSO_4$) (shown in reactions (1)–(3)) [1,2]. Lead dioxide is a semiconductor with a conductivity of about 50 Ω^{-1} cm^{-1} in battery electrodes [3], whereas $PbSO_4$ is non-conductive. It is important to note that the positive electrode does not pacify; during discharge a layer of $PbSO_4$ accumulates on the positive plate, but both HSO_4^- and H^+ traverse this porous layer [4,5]. However, during discharge, nodules of PbO_2 become electrically isolated (Fig. 1), preventing complete reaction of all active material [6,7].

Positive plate:

$$\mathrm{Pb^{(IV)}O_2 + HSO_4^- + 3H^+ + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Pb^{(II)}SO_4 + 2H_2O,}$$

$$E^0 = 1.805\,\mathrm{V} \tag{1}$$

Negative plate:

$$\mathrm{Pb^{(0)} + HSO_4^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Pb^{(II)}SO_4 + H^+ + 2e^-,}$$

$$E^0 = -0.340\,\mathrm{V} \tag{2}$$

Total:

$$\mathrm{PbO_2 + Pb + 2HSO_4^- + 4H^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O,}$$

$$E^0_{\text{cell}} = 2.145\,\mathrm{V} \tag{3}$$

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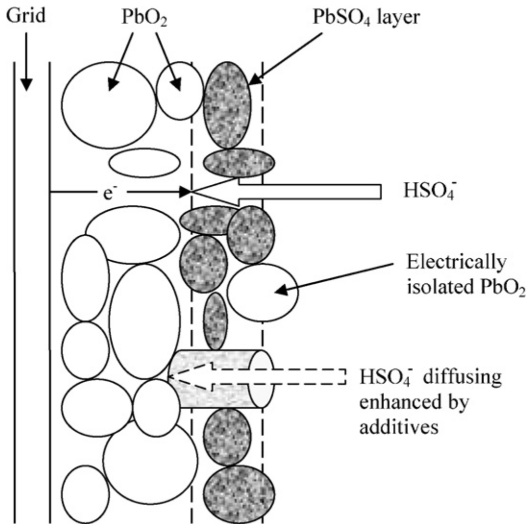

Fig. 1. Diagram of porous lead dioxide paste with diffusion of acid.

Currently, lead-acid batteries operate at very low positive active material (PAM) utilization, typically around 30% at the 1 h rate [8]. Compared to the negative plate, the positive plate is performance limiting [9–13], and therefore much research has been done to improve its capacity by adding positive plate additives. Low PAM utilization can be attributable to poor mass transport of sulfuric acid to the interior of the active material (PbO_2) and an increase in the formation of non-conductive $PbSO_4$ [12,14]. Due to the amount of non-reacted material in the form of isolated PbO_2, the specific capacity of the battery is low. These problems can be minimized by adding porosity and conductivity enhancing additives to the PAM, or by replacing the unreacted paste with additive. These approaches have been studied by many investigators [13–17].

Porous additives increase the supply of $HSO_4{}^-$ and also provide local reservoirs of this ion within the pores [13]. Fig. 1 illustrates ion conduction through the pores to the inside of the active mass. Because lead-acid batteries have harsh chemical and oxidative conditions, the following characteristics must be considered while selecting an additive [14]:

- chemical and oxidative stability;
- maintain cohesion of paste;
- increase PAM utilization without affecting cycle life;
- inexpensive;
- light weight.

Previous investigations have found that the addition of hollow glass microspheres enhance utilization by increasing the ratio of available H^+ and $HSO_4{}^-$ to active material by replacing unreacted active material with additive [18]. Positive plates with 0, 2.2, 4.4, and 6.6 wt.% of glass microspheres were studied. At high discharge rates (i.e. 0.1 A g^{-1}) the maximum utilization of 33.12% occurred with 4.4 wt.% additive. This was an improvement over the production plate with no additives, which had a utilization of 11.46%. Despite the better utilization, the disadvantage of using this approach is that the additive increases the battery volume, which in turn decreases the battery's energy density (energy per volume).

Carboxymethylcellulose (CMC) and silica gel were also studied as porosity enhancing additives [15]. The CMC increased the water absorption of the paste and increased the initial capacity of the plate. However, due to CMCs swelling and removal by oxidation, the mechanical strength of the plate was decreased, which resulted in poor cycle life. Also found was that an addition of 0.2 wt.% silica gel with size 30–150 nm increased capacity over 10% (from 33.3% to 37.2% utilization) with no change in cycle life [15]. It was assumed that since silica gel is quite porous, the additive acted as an acid reservoir [15].

In a different study with silica, the initial capacity was low due to the replacement of some of the active material, but the SiO_2 additive reduced the capacity loss from cycling [19]. Other studies using porous silica beads as additives found they gave high initial capacity and good performance at a high discharge rate [19–21].

In this work, diatomites were selected as a positive electrode additive due to their porosity, stability, and abundance [22,23]. Previous uses of diatomites include enhancing porosity in lead-acid battery separators by mixing diatomites with a polymeric separator material such as latex or polyethylene [22–24]. Toussaint et al. used zeolite, ZSM-5 type (Utikon-zeochem), a diatomite family with a pore diameter close to 0.5 nm, as an additive for compressed cells. The addition of 1 wt.% showed an increase in capacity (Ah kg^{-1}) of close to 20% [25]. However, there have been no investigations on the effect of particle size on performance in the literature. For this investigation, we examined and reported the effects of size sorting of diatomites on PAM capacity.

2. Experimental

2.1. Apparatus

All electrochemical procedures were done on either a MSTAT 8 channel potentiostat (Arbin Instruments, College Station, TX), or a PC4/750 (Gamry Instruments, Warminster, PA). Formation was done against a commercial negative plate (Concorde Battery Corporation, West Covina, CA). Cycling tests were completed using a flat cell (Princeton Applied Research, Oak Ridge, TN) and a three electrode system, with the lead dioxide positive paste as the working electrode, Ag/AgCl reference (3 M NaCl, Bioanalytical Systems, Inc., West Lafayette, IN), and a coiled platinum wire (Alfa Aesar, Ward Hill, MA) as the counter electrode.

2.2. Diatomite additive

As an additive, diatomites (Melosira) were selected and obtained at a local hardware store. Because of the size variation in the unsorted diatoms, they were filtered through a nylon sheet (Small Parts, Inc., Miami Lakes, FL) before addition into the paste mixture. In this manner we were able to obtain results with varying weight percentages as well as different size fractions.

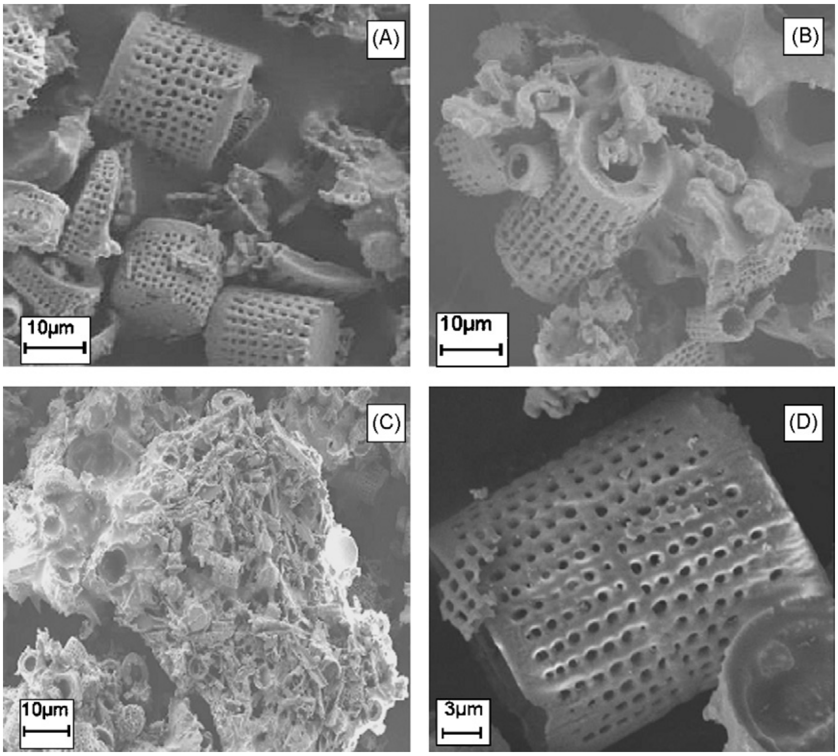

Fig. 2. Scanning electron micrograph of diatoms of different sizes (A) 20–30 μm, (B) 53–74 μm, (C) >90 μm, and (D) diatoms recovered from active material after the performance tests.

2.3. Paste preparation

The paste was prepared by hand, with the diatomite additive dry mixed into PbO (Concorde Battery Corporation, West Covina, CA) prior to water and sulfuric acid addition. Batches were made up to a total mass of 10 g dry weight, each composed of 0.5% shredded Dynel® fiber, 0–5 wt.% diatomite additive (Fig. 2), with the balance made up with PbO. 1.2 mL of water was added over several minutes while mixing, followed by 1 mL of 1.4 specific gravity sulfuric acid (Fisher Scientific, Pittsburgh, PA) slowly dripped into the mixture while continuing to mix. Additional water was added to this paste until a workable texture was obtained and the paste mass stopped increasing. The paste was packed into Teflon® rings (Princeton Applied Research, Oak Ridge, TN) glued to 4–6% antimony–lead (McMaster-Carr, Santa Fe Springs, CA) sheets cut into strips (Fig. 3). The Teflon® rings have an inside volume of 0.24 mL and, when filled with the paste, provide an exposed area of 1 cm^2. A total of five positive electrodes were produced.

Curing was performed in a pressure cooker at 100% humidity and 121 °C for 24 h. Electrodes were then dried at 38 °C overnight and weighed to determine the mass of the paste. The mass of the paste was usually between 0.6 and 0.8 g, depending on the composition.

After curing, one of the electrodes was tested for porosity and Pb^0 content. The porosity test was performed by water absorption, measuring the weight of the paste before and after water has been absorbed. If the porosity was less than 45%, all the electrodes in the batch were discarded. Zero-valent lead was determined if the electrode had adequate porosity (≥45%). A sample of 0.2 g of the paste was dissolved in 15 mL of 40% acetic acid (Mallinckrodt Baker, Inc., Phillipsburg, NJ). After sonicating for 30 min, ammonium hydroxide (Fisher Scientific, Pittsburgh, PA) was added until the solution cleared and the solution was sonicated for 15 more minutes. This treatment dissolved both the lead oxide and the lead sulfate, leaving the unconverted Pb^0 at the bottom of the flask. The lead particles were then dissolved in 10% nitric acid (Fisher Scientific, Pittsburgh, PA) before the concentration of lead was determined by an atomic

Fig. 3. Pasted electrode after curing. Internal volume of Teflon® ring is 0.24 mL.

Table 1
Percent change in utilization for fast (50 mA cm^{-2}) and slow (10 mA cm^{-2}) discharge rates relative to control samples

Fast/slow	20–30 μm		30–53 μm		53–74 μm		74–90 μm	
3%	−5.0%	−10.0%	−9.0%	−6.8%	12.7%	3.7%	−1.3%	6.7%
5%	−2.8%	10.6%	−0.9%	11.5%	4.6%	−4.2%	4.2%	−0.2%

Table 2
Percent change in capacity for fast (50 mA cm^{-2}) and slow (10 mA cm^{-2}) discharge rates relative to control samples

Fast/slow	20–30 μm		30–53 μm		53–74 μm		74–90 μm	
3%	−7.9%	−12.7%	−11.7%	−9.6%	9.3%	0.6%	−4.3%	3.5%
5%	−7.7%	5.0%	−5.8%	5.9%	−0.7%	−9.1%	−1.0%	−5.2%

absorption spectrometer (Perkin Elmer—Model 5100 PC, Norwalk, CT). If the paste contained more than 5 wt.% Pb^0, the rings were wet with sulfuric acid and cured again.

2.4. Formation and conditioning

Formation was started by charging the rings to 100% of their stoichiometric capacity over 24 h and then charging at half that rate for 12 h in 1.1 specific gravity (s.g.) acid against a negative plate. Due to a tendency of the paste to lift off the plate, slight pressure was applied to the paste using a glass mat separator. No pressure was applied otherwise. After formation to 125% capacity, the acid was replaced with 1.3 s.g. and charged for 6 h at the low formation rate. The electrodes were conditioned by cycling them five times using a discharge of 10 mA g^{-1} active material and charged at the 24 h rate to 125% of the discharge capacity.

2.5. Performance measurements

A group of electrodes with no additives were pasted as our control samples. Four groups with diatomite sizes 20–30 μm, 30–53 μm, 53–74 μm, and 74–90 μm were pasted with 1, 3, and 5 wt.% loadings. Four electrodes in each group were tested. Capacity measurements were taken at 50 mA cm^{-2} discharge and 10 mA cm^{-2} discharge to a cut-off voltage of 1.3 V (versus Ag/AgCl). Electrodes were cycled at each rate until the capacity reached a maximum. All tests and procedures were carried out at room temperature and pressure.

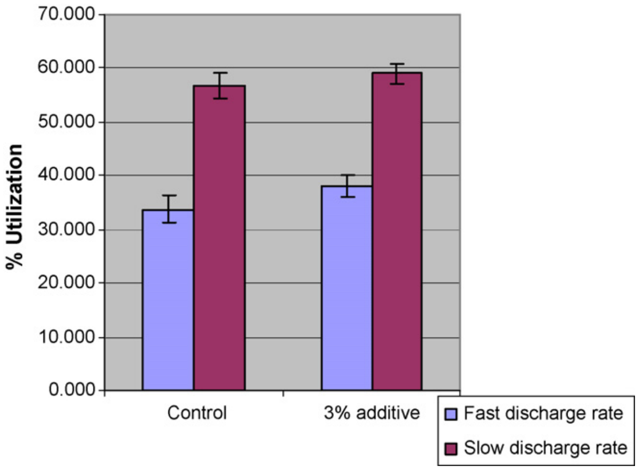

Fig. 4. Utilization of 3 wt.% 53–74 μm diatomite compared to paste with no additive.

3. Results

Scanning electron micrographs (SEM) (Fig. 2A and B) show the porous structure of diatomites. Fig. 2C shows the SEM of diatomites of particle size greater than 90 μm, which were not used due to their size and solid appearance. The effect of porous diatomites on the utilization of active material both at 50 mA cm^{-2} and 10 mA cm^{-2} discharges were measured. Tables 1 and 2 lists the percent change in utilization and specific capacity (mAh g^{-1}) for fast (50 mA cm^{-2}) and slow (10 mA cm^{-2}) discharge rates relative to a control plate with no additive. The plate with 53–74 μm diatoms at both 3 wt.% and 5 wt.% concentrations had the best performances. Tests were not conducted with 20–30 μm or the 74–90 μm sizes at 1 wt.% loadings of diatomites as those sizes did not perform well at the 3 wt.% and 5 wt.% loading. After the performance tests, we recovered diatomites from the active material for SEM analysis. As can be seen, their structure was not affected (Fig. 2D), confirming that diatomites are stable in the battery environment.

4. Discussion

The addition of 3 wt.% diatomite exhibited the best performance of the weight distributions studied (Fig. 4). This is in close agreement with studies by Edwards et al. on glass microspheres [18]. At ratios above 5 wt.% the positive plate lost mechanical stability and particles were observed to slough off.

The 53–74 μm size diatomites (Fig. 2B) exhibited the largest increase in utilization and capacity at fast discharge rates (50 mA cm^{-2}) (Tables 1 and 2). Single diatomite elements shown in Fig. 2A did not perform as well as conglomerates in Fig. 2B. This is probably based on the conglomerate's ability to enhance acid mass transport within the PAM without being filled in. Single elements were observed to be filled with PAM; however, it is possible that the voids between the elements within conglomerates remain open and allow acid conduction.

An examination of Tables 1 and 2 show an increase in capacity during slow rate discharge. These increases are determined to be insignificant due to the amount of variation in the collected data. Data is considered statistically unique only if error bars consisting of the standard deviation do not overlap those of the control group.

5. Conclusion

Diatomites are inexpensive filler material that increase positive active material utilization by (i) replacing unreacted active material, while (ii) maintaining pores for acid transport. With naturally occurring porosity and stability in lead-acid battery conditions, diatomites are a suitable choice as an additive. When 3 wt.% of diatoms are added to the paste prior to pasting, utilization increases by over 12% at a fast rate discharge of 50 mA cm^{-2}. There is also a corresponding increase in specific capacity, with a 9% increase when capacity is normalized to total weight of the paste, including additive. Based on the results of this investigation, future research will include the use of full size plates in order to verify that the performance enhancement with small scale positive plates will carry over to full size and possibly compressed cells.

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