



Short communication

Investigation on electronically conductive additives to improve positive active material utilization in lead-acid batteries

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ARTICLE INFO

Article history:

Received 2 December 2008

Received in revised form 16 December 2008

Accepted 17 December 2008

Available online 30 December 2008

Keywords:

Active material utilization

Conductive additives

Lead-acid battery

Positive electrode

Titanium

ABSTRACT

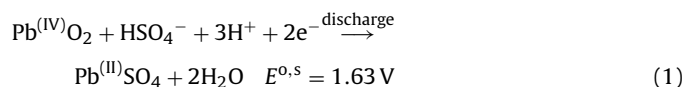
In order to adapt lead-acid batteries for use in hybrid electric vehicles, its specific energy must be improved. Specific energy is greatly dependant on active material utilization. In this study, we improve active material utilization in positive electrodes by the addition of electronically conductive additives. Titanium silicide particles (<44 μm diameter), titanium dioxide fibers (<10 μm, diameter), and titanium wire (76 μm, diameter) were incorporated into the positive electrode and each of their effects on discharge capacity and utilization of active material were examined. The percent mass of each additive was varied from 2–5%. Results indicate that titanium wire at 2.3 wt.% had the optimal effect of increasing the utilization by 12.3% (57 to 64% utilization) relative to control with no additive at a slow discharge rate (10 mA cm⁻²) without detrimental effect at fast discharge rate (50 mA cm⁻²). This additive also features reduction in weight and formation enhancement.

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1. Introduction

In hybrid electric vehicle applications, Li-ion and nickel-metal hydride batteries have predominated [1–3]. However, the lead-acid battery system is more promising in applications to this field because of its low cost and robust nature [3,4]. Lead-acid batteries (LABs) offer a number of advantages over more advanced battery designs [5]. First, LABs generate high power density which is desirable for acceleration and start-up. Second, LABs have a well established manufacturing and recycling system that reduces the cost of production, and lowers its environmental impact. In addition, the raw materials in LABs are cheaper than those for newer battery types. Third, modern LABs are sealed, with no spilling or gassing during normal use [5]. The disadvantage is that the specific energy of lead-acid batteries is too low to be used in hybrid electric vehicles where pure electric range is required, therefore current LABs are limited to use in medium hybrids [4]. On a practical basis, a lead-acid battery generates approximately 30 Wh kg⁻¹, compared to a theoretical specific energy of 167 Wh kg⁻¹ indicating possibilities for improvements [6]. In comparison, nickel-metal hydride and lithium-ion batteries have specific energies between 65–75 and 100–150 Wh kg⁻¹, respectively [6].

The low specific energy is attributable to poor utilization of active materials (Pb and PbO₂) [6]. Utilization is defined as the ratio of ampere hours discharged to the stoichiometric capacity of the active material. There has been much focus on the positive electrode of the lead-acid battery as it has 5–10% lower utilization than the negative electrode [7–11]. The basic electrochemical reaction of the positive electrode is shown below: [12,13]



As evident in Eq. (1), PbO₂ is converted to PbSO₄ during discharge, which is reversed upon charging. However in practice, the charge and discharge reactions are incomplete [11]. The utilization of positive active material (PAM) is mainly limited by two effects (illustrated in Fig. 1A and B):

- Poor mass transport of electrolyte through the PbSO₄ layer of the positive electrode [8].
- Electronic isolation of PbO₂ due to the formation of a surrounding non-conductive PbSO₄ layer as well as an overall decrease in conductivity [8,11,14–16].

It is noteworthy to add that there are two more effects which detract from PAM performance. In a process known as sulfation, a permanent non-conductive layer of PbSO₄ can be formed [11]. Active material utilization is also limited by an imposed but nec-

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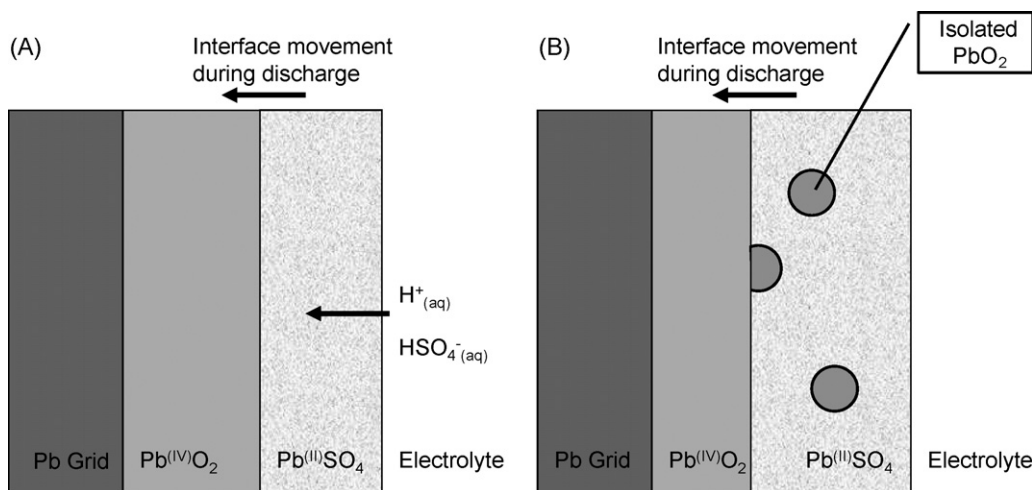


Fig. 1. A and B illustrates the situation outlined in (a) and (b).

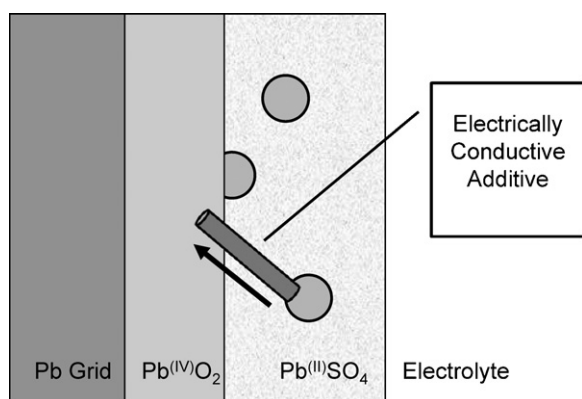


Fig. 2. Electrically conductive additives bridging isolated active material, thus increasing utilization.

essary cut-off potential (varies depending on discharge rate) at which considerable amount of PbO_2 remains unreacted [17]. Cut-off potential is necessary as the lifetime of a lead-acid battery is adversely effected by complete discharges [12].

When considering the effects of (a) and (b) it is important to consider that active material utilization is influenced by discharge rate [18,19]. At fast rates (1 h rate, 50 mA cm^{-1}), the positive plate reaction is limited by mass transport of HSO_4^- [20]. At slow rates (10 h rate, 10 mA cm^{-1}), the capacity of the positive plate is mainly limited by electronic conductivity of the active material [11,21].

In previous studies, additives that enhance ion-conductivity, such as diatomaceous earths [16], were added to increase H^+ and HSO_4^- transport into the positive electrode thereby increasing active material utilization at fast discharge rates [22,23]. Insofar as isolated PbO_2 , several researchers have suggested that electronically conductive additives may ameliorate this problem [8,14,18]. Fig. 2 illustrates how the electronically conductive additives may serve as a pathway that connects isolated PbO_2 to the Pb grid. For a

positive plate an electronically conductive additive must have conductivity greater than lead sulfate and preferably as good as lead dioxide ($50 \Omega^{-1} \text{ cm}^{-1}$) [8,24]. There are also other important considerations in selecting an electronically conductive additive for the PAM of the lead-acid battery: [8,16]

- i) Stability in both the harsh chemical and high oxidation potential of positive plate,
- ii) Good mechanical strength and cohesion for prolonged cycle life,
- iii) Good geometrical shape for conductive network,
- iv) Low cost, and
- v) Light weight.

1.1. Previous research on conductive additives

A literature search yields many examples of conductive additives. Kao and Bullock used barium metaplumbate (BaPbO_3 , $10^{-4} \Omega \text{ cm}$ [25]) which increased the formation efficiency [26]. However, barium metaplumbate is not stable in sulfuric acid and does not increase utilization. Wang et al. found that 0.5 wt.% of graphite added to the positive electrode enhanced the utilization by about 15% during initial cycles [27]. Carbon fibers, needle coke, and polyacene were also tested in the positive paste [27]. These carbon based additives oxidize to CO_2 during cycling and therefore are not beneficial in the long term. Magnelli phases of oxides of Ti ($\text{Ti}_n\text{O}_{2n-1}$) and W suboxides (WO_{3-x} , where $0 \leq x \leq 1$) are known to be very conductive [8,20]; however, titanium suboxides decomposes in sulfuric acid and tungsten suboxides are unstable in positive electrode potentials [28]. Kao selected 60 different materials and tested them for stability in sulfuric acid and battery potentials [28]. Among them, only SnO_2 , TiSi_2 , TaSi_2 , and NbSi_2 remain effective in these highly corrosive conditions.

Tin dioxide coated glass flakes were used in positive plates in order to increase the conductivity of the paste by Lam et al. [18]. A 2 wt.% loading of 1/64 inch and 1/8 inch glass flakes were investigated. Overall, the authors concluded that the larger flakes provided

Table 1
Selected additives for the positive electrode.

Additive	Resistivity ($\Omega \text{ cm}$)	Size	Loading (wt.%)	Supplier
PbSO_4	10^8 [6]			
TiSi_2	10^{-6} [30]	<44 μm	3%	Alfa Aesar (99.5%)
TiO_2 fiber	10^{12} [31]	<10 μm dia.	3%	Self synthesized ¹ [32]
Ti wire		76 μm dia.	2.3%	Alfa Aesar

¹Titanium dioxide fibers were synthesized using the procedure presented by Aminian et al.

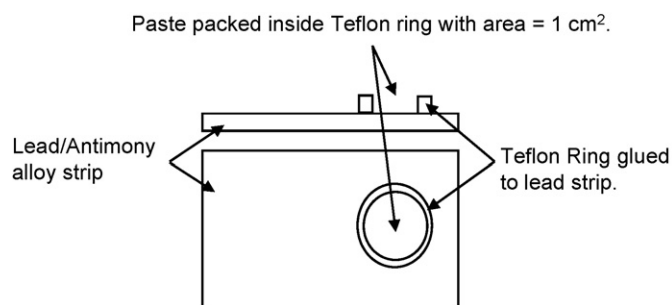


Fig. 3. Representation of the positive electrode used in this study. The rings were 2.2 mm deep.

more benefit than the smaller ones [18]. In addition to improved paste formation, the additive was able to demonstrate increased utilization with capacity increases of 2–31% and greater cycle life [18]. Similarly, Hariprakash et al. [29] coated 3 mm by 25 μm Dynel fibers with tin dioxide, and added 2 wt.% to their positive paste. The test cells with the additives showed increases in both utilization and capacity of 15–25%, depending on the discharge rate, as well as reduced formation times. In addition, using electrochemical impedance measurements and equivalent circuit modeling, they concluded that the charge transfer resistance is lower in plates with the conductive fibers [29].

The effects of geometric shape and size of additives on the utilization of PAM was studied by Edwards et al. [14,15,21]. A 2D model was used to study the effects of different particle sizes and aspect ratio (ratio of length to diameter) of additives on the critical volume fraction. Their model indicates that small conductive particles would provide higher utilization than large conductive particles at equal loadings because of better dispersion. It was also shown that the longer, higher aspect ratio conductive additives can bridge more isolated areas than spherical particles and thus could effectively improve utilization of active material.

1.2. Additives selected for this study

In this work, various forms of titanium were used to enhance electronic conductivity of the positive paste. The list of electronically conductive materials selected for our positive electrodes are shown in Table 1. Titanium silicide was selected for its low cost as well as its durability in sulfuric acid and oxidative potentials. Titanium wire and TiO_2 fibers were chosen for their high aspect ratios.

2. Experimental procedure

Positive electrodes were fabricated with 1 cm^2 surface area and 2.2 mm depth. The paste preparation was similar to the procedure shown in our previous work [16]. Pastes were prepared in batches with different types of additives as given in Table 1. Each batch included 4–5 electrodes of the same composition. The paste was made to a total dry mass of 10 g with 0.5 wt.% shredded Dynel® fibers, 0–5% additives, and leady oxide (PbO and Pb). After dry mixing, 1.2 mL deionized water and then 1 ml 1.4 specific gravity sulfuric acid were slowly mixed in. Additional water was added until the density reached a maximum to produce proper consistency for pasting. The additives were used as purchased or synthesized, although the titanium wire was chopped 1–2 mm in length before being added to the dry paste. The positive pastes were applied evenly inside Teflon® rings glued to 4–6% antimony-lead strips as shown in Fig. 3. The Teflon® rings were used in order to hold the paste, as well as give the electrodes a defined size and shape. Pasted electrodes were then cured in a pressure cooker for

Table 2

Percent change in utilization for fast (50 mA cm^{-2}) and slow (10 mA cm^{-2}) discharge rates relative to control. Four electrodes tested.

Additive type	TiSi_2	TiO_2 fibres	Ti wire
Loading (wt.%)	3%	3%	2.3%
Fast discharge– 50 mA cm^{-2}	–9.1%	9.9%	13.6%
Slow discharge– 10 mA cm^{-2}	4.3%	–1.2%	12.4%

Table 3

Percent change in specific capacity (mAh g^{-1}) for fast (50 mA cm^{-2}) and slow (10 mA cm^{-2}) discharge rates relative to control. Four electrodes tested.

Additive type	TiSi_2	TiO_2 fibres	Ti wire
Loading (wt.%)	3%	3%	2.3%
Fast discharge (50 mA cm^{-2})	–11.9%	6.7%	12.3%
Slow discharge (10 mA cm^{-2})	1.1%	–4.2%	9.8%

24 h at 100°C at a relative humidity of 100%. The electrodes were then dried overnight to determine the final weight of the paste. After curing, one of the pasted electrodes was tested for porosity using water absorption and the concentration of Pb^0 was determined using atomic absorption spectrometer [16]. If the porosity was less than 45% all the plates in the batch were redone. Pb^0 content was used to test for the completion of the curing process. If there was greater than 5% Pb^0 , then the plates were cured for an additional 24 h.

A constant electrochemical forming method was adopted. Theoretical capacity was calculated as 0.2241 Ah g^{-1} based on the weight of the paste. The positive electrodes were galvanostatically charged for 30 h at 9.34 mA g^{-1} (24 h rate) to 125% theoretical capacity. This was followed by charging for an additional 12 h at 4.67 mA g^{-1} (48 h rate), for a total charge of 150% theoretical. Formation was done with a commercial pre-formed negative plate in 1.1 specific gravity sulfuric acid. Polyethylene separators were placed between positive plates and negative plate. Glass mat separator with 90% porosity was used to provide slight back pressure in order to prevent the paste from lifting off the plate.

Discharge was carried out in a three electrode flat cell which contained 1.3 specific gravity sulfuric acid. The working electrode was the positive electrode, with only the positive paste exposed to the electrolyte solution. The antimony-lead strips were used for structural support as well as the electron carrier. The counter electrode was a platinum wire, and the reference was a Ag/AgCl electrode ($E=209\text{ mV}$ vs. NHE). During the capacity tests, no electrolyte was seen leaking from the Teflon® rings. Cycling was done under computer controlled charge and discharge regimens using commercially available cycling equipment. Each electrode was charged at 4.67 mA g^{-1} (48 h rate) for 3 h and then conditioned with cycling at a discharge rate of 10 mA g^{-1} of active material and charged at 9.34 mA g^{-1} to 150% of the previous discharge capacity. The end of discharge potential was limited to 1.3 V vs. Ag/AgCl . Finally, discharge capacity measurements were carried out at a fast discharge rate of 50 mA cm^{-2} and at a slow discharge rate of 10 mA cm^{-2} . Reported results were after maximum capacity had been achieved for each batch of electrodes. Positive electrodes without any additive were used as our control samples.

3. Results

The effect of each additive on the utilization of active material was examined by comparing their maximum capacities with that of the control samples. Control samples had $33.8 \pm 2.5\%$ and $56.9 \pm 2.5\%$ utilization at 50 mA cm^{-2} and 10 mA cm^{-2} , respectively ($n=8$, error is 1 standard deviation). The change in utilization and specific capacity for the positive electrodes with additives were calculated relative to the control and are presented in Tables 2 and 3.

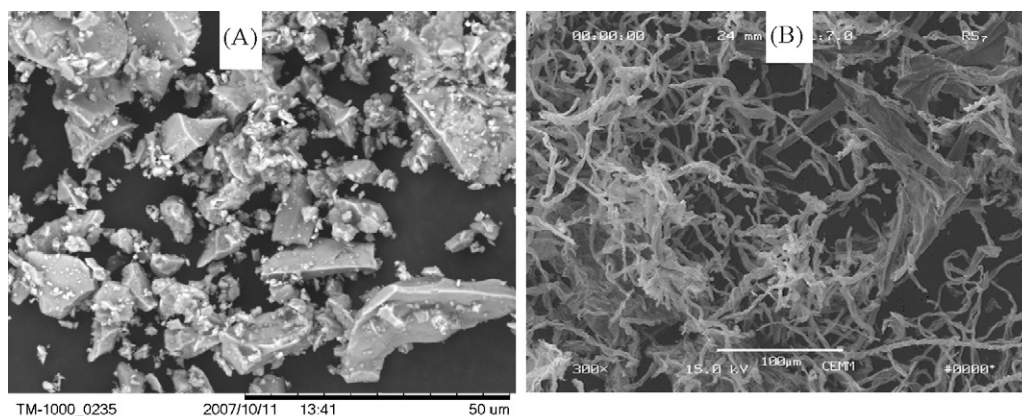


Fig. 4. SEM of (A) TiSi₂ < 44 μm particle size (B) TiO₂ fibers < 10 μm dia. Both additives are shown before being added to paste.



Fig. 5. Ti wire (76 μm dia.) in positive paste taken after cycling tests. Optical microscope at 4× magnification.

Results reported for TiSi₂ and TiO₂ had errors that overlapped with that of the control so are considered not significant. Only Ti wire additive electrodes had significant improvements. The reported loadings had the maximum positive change in utilization. Titanium wire at a 2.3 wt.% loading had utilization of $38.3\% \pm 2.1\%$ and $63.9\% \pm 3.6\%$ at 50 mA and 10 mA discharges, respectively. Other loadings tested (from 0–5 wt.%) are not reported. Loading of additives did not exceed 5% because there was significant amount of shedding of the positive paste, making these results unreliable.

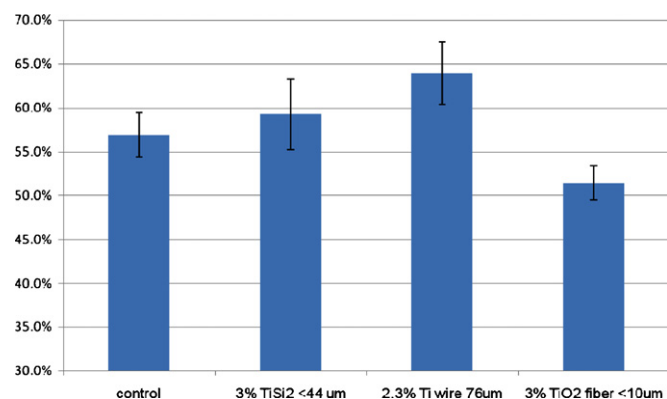


Fig. 6. Percent utilization for the positive electrode systems examined for this study at 10 mA cm⁻². The control contained no additives. Error bars represent one standard deviation unit for $n = 4$.

Fig. 4 shows the scanning electron micrographs (SEM) of TiSi₂ particles and TiO₂ fibers before being added to the paste. Fig. 5 presents the SEM of Ti wire embedded in the positive paste after 3 weeks of cycling. A SEM of the cured positive electrodes with the TiO₂ fibers showed no evidence of any fibers surviving the process.

4. Discussion

Utilization values are reported in this study in order to facilitate comparisons with our previous work on porous additives [16] as well as with utilization models [21].

Although TiSi₂ is reported to have metal like conductivity [28], it did not show significant increase in the utilization of the PAM. However, the conductivity of the titanium silicides sample used in this study was not examined. Other variables of importance include particle size, loading, and aspect ratios that have not been optimized [21]. TiO₂ fibers ($d < 10 \mu\text{m}$) were not found to be durable in the PAM as revealed by electron micrographs. This may be due to mechanical stresses during the pasting process which may break the fibers down into fine dispersed powder. All three additives, i.e. TiSi₂, TiO₂, and Ti are stable in the paste.

Increased shedding at high loadings of additives may be caused by less PAM holding the paste together. Other possibilities include that the additives change the structure of the PAM or do not adhere well to the lead substance. As this was a preliminary study of how certain additives effect PAM utilization, no cycle life tests were done.

Although titanium wire completely dissolves in 1.3 specific gravity sulfuric acid in a couple of days, this additive was found to be durable under the prevailing conditions of the PAM paste for 3 weeks of testing. They showed a significant increase in utilization of 12.4% at slow discharge rate (Fig. 6), as well as a 13.6% increase in utilization at fast discharges. This result correlates well with the 2D model of Edwards and Zhang [21]. The model predicts that even with a low loading, a long conductive additive (1×100 aspect ratio) should raise the utilization from around 60% to between 65–70% [15,21]. The phase composition of titanium wire at different locations on the positive electrode was determined by X-ray diffractive spectroscopy (EDS). The results indicated 98 wt.% titanium even after 40 cycles. Because Ti is soluble in sulfuric acid, it is possible there are Ti ions in the electrolyte, but due to the increase in capacity of electrodes with Ti, it seems that the Ti ions in solution does not detrimentally affect the performance of the PAM. The cost for titanium wire prohibits commercial use as an additive for lead-acid batteries, but our research supports the hypothesis that high aspect ratio additives can have a positive effect on positive plate utilization [21].

5. Conclusion

Titanium wire is light weight and has a high aspect ratio so that it can serve as a conductive network over greater distances within the positive paste. The titanium wire increased the active material utilization by over 12% at the slow discharge rate, without detrimental effects on utilization during the fast discharge rate which showed a 13.6% improvement. The studies of SEM and EDS analysis revealed that the titanium wire is stable in the positive electrode conditions for over 40 cycles with no evidence of a decrease in size. However as titanium wire is expensive, more cost effective methods should be developed. Future research should include (i) locating durable conductive additives with a high aspect ratio and (ii) addition of a combination of porous diatomaceous earth particles and conductivity enhancing additives in the positive paste to study its influence on electrode performance.

Acknowledgements

Office of Naval Research Award Number: N00014-04-1-0612, University of Idaho Department of Chemistry, Dr. and Mrs. Renfrew summer scholarship support, Microelectronics Research and Communications Institute (MRCI) of University of Idaho.

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