

Beneficial effect of carbon–PVA colloid additives for lead–acid batteries

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Abstract

Based on the previous success of adding ultra-fine carbon–PVA (polyvinyl alcohol) colloid solution to restore performance of weak batteries, a large scale test programme of practical batteries including those used in forklift, golf cart, taxi cab, truck and bus applications from 150 companies was carried out. More than 95% of the tested batteries exhibited excellent recovery in performance parameters including the specific gravity (S.G.), voltage and operation time (Ah capacity). The work reported here includes basic research studies to understand better the beneficial action of the carbon–PVA colloid additive. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The beneficial action of UFC (ultra-fine carbon) and PVA (polyvinyl alcohol) composite colloid for preventing discharge capacity deterioration of lead–acid batteries was reported previously [1,2]. Originally, it was thought that the carbon material was solely responsible for the improvements, acting as a deposition site for lead during charge. Based on the laboratory tests, the UFC–PVA additive has beneficial action, mainly for the sulfated negative electrodes. The additive facilitates the generation of good active lead from damaged negative electrodes. It was concluded that most of the battery deterioration was due to the sulfation of the plate. Antimony from positive grid corrosion was deposited on the negative electrode. This lowered the hydrogen overvoltage and prevented the negative from accepting a full charge. The test results on a 3-year-old 640 Ah forklift battery suggest that the PVA also played an important role in the restoration of good performance [3]. It was postulated that PVA forms a

complex with the Pb^{+2} ions in solution and this complex facilitates the deposition of active lead. The PVA may also raise the hydrogen overvoltage and allow the plate to accept full charge.

It is appropriate to demonstrate the effectiveness of the additive on a larger scale and for a variety of battery types. In this paper, large-scale test results of practical lead–acid batteries ranging from 50 to 620 Ah are described. The excellent recovery of specific gravity (S.G.), voltage and capacity was observed for more than 95% of the tested batteries.

2. Batteries tested and the test procedure

Table 1 shows typical batteries tested and their average life. The state of the batteries ranged from 60 to 70% of their expected life at the time the testing was initiated. The UFC-colloid solution was added to each cell of the battery. The addition of the UFC-colloid was carried out in the same manner as for water addition to lead–acid batteries. The cap on each cell was unscrewed, the additive poured

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Table 1
Status and types of batteries tested from various companies

Type	Capacity, Ah	Number of companies	Useful life, years ^a
forklift batteries	280 to 545	50	4 to 5
golf cart batteries	50 to 130	15	2 to 3
construction equipment	65 to 130	15	2 to 4
taxi cab	55 to 75	15	1.5 to 2
truck, bus, diesel car	130 to 150	15	3 to 5

^aThis value depends on each company's use pattern.

into the top of the cell, and the cap replaced. The battery was then returned to service.

The UFC–PVA colloid solution used in the testing contained 5% by weight of the solid carbon–PVA colloid material. The solution consisted of carbon black (0.15 μm) and PVA in the weight ratio of 10:4. The details of the composition and stability have been reported [1]. Since 5% by volume was added to each cell, the net amount of colloidal solid carbon added was roughly 0.25 g per 100 ml of electrolyte.

Before addition, the batteries were inspected for obvious flaws. The owner of the battery supplied the age of the battery. The S.G. and voltage of each cell were measured after full charge. After addition, the batteries were returned to operation on the same use pattern as before. Every 1 or 2 weeks, the S.G. and voltage were measured for a period of up to 3 months.

3. Results

Typical changes of S.G. are shown in Figs. 1 and 2 for a forklift battery and a golf cart battery, respectively. In the case of forklift batteries, the hours of operation increased noticeably. The forklift battery also gave noticeably better performance on lifting heavy loads. The change of S.G. was observed in 2–3 weeks after the addition of the UFC-colloid for deep charge–discharge batteries such as forklift and golf cart.

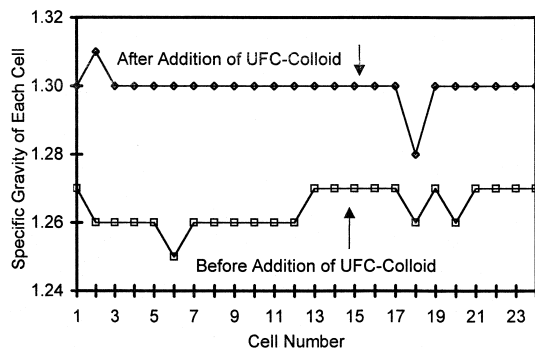


Fig. 1. Specific gravity of a 400 Ah, 48 V forklift battery before and after addition of UFC-colloid solution. Curve A: Before addition on January 23, 1998. Curve B: After addition, March 4, 1998.

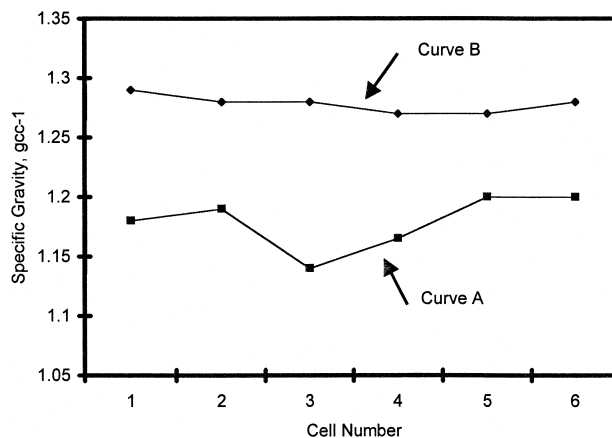


Fig. 2. Specific gravity of a golf cart battery left unused for 40 days. Curve A was taken before addition of UFC-colloid on April 2, 1998, when daily use started. Curve B was taken on June 9, 1998 after addition of UFC-colloid.

In the case of buses and trucks, the increase of the S.G. value was very slow. It took 2–3 months before a noticeable change in the S.G. took place. Fig. 3 shows typical behaviour of the S.G. with time for a 128 Ah truck battery after addition of the colloid. In some cases, the battery performance was poor even though the S.G. was high (1.28–1.30). These batteries also recovered their performance with the UFC–PVA colloid additive.

Figs. 4–6 show the test results of aircraft-engine starter batteries (620 Ah, 30 V). These batteries are used to start the engine during ramp service operations. The S.G. of the electrolyte remained around 1.275 for a period of 2.2 years from March 28, 1995 to August 5, 1997 but it began to drop around October 20, 1997 as shown in Fig. 4. Upon addition of the UFC-colloid the S.G. value jumped back to 1.28 in a month. During that time, the battery continued in normal use for engine starting with a normal charge regime. The temperature during the charge increased gradually to

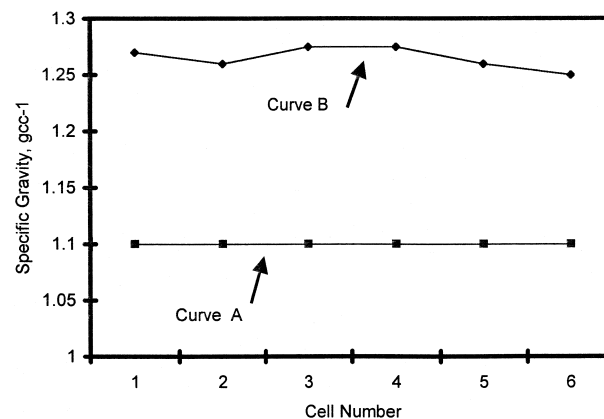


Fig. 3. Specific gravity of a 128 Ah, 12 V truck battery. Curve A was taken before addition on January 14, 1998, when daily use started. Curve B was taken on January 22, 1998, after addition of UFC-colloid.

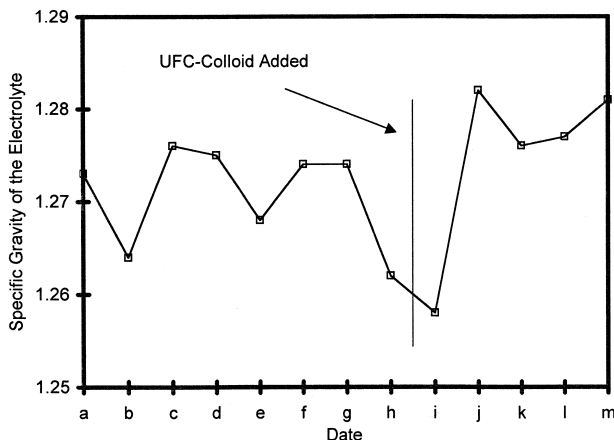


Fig. 4. Change of specific gravity of the electrolyte with time for a 620 Ah 30 V aircraft-engine starter battery. Readings were taken on the following dates: (a) March 28, 1995; (b) Oct. 2, 1995; (c) April 1, 1996; (d) Oct. 4, 1996; (e) April 5, 1997; (f) June 10, 1997; (g) Aug. 5, 1997; (h) Oct. 3, 1997; (i) Oct. 22, 1997; (j) Nov. 12, 1997; (k) Dec. 11, 1997; (l) Jan. 21, 1998; and (m) Feb. 28, 1998.

40°C before addition of the UFC-colloid. After the addition, it dropped back to 22°C. Fig. 6 shows the current–voltage curves before and after the addition of UFC-colloid. The additive noticeably improved the high rate capability.

4. Discussion

The increase of the S.G. value of the H_2SO_4 electrolyte means that inactive $PbSO_4$ accumulated in the negative electrode dissolved and converted back to active lead and sulfuric acid. An increase in S.G. was observed in more than 95% of the tested batteries from the 150 companies. This means that the cause of battery deterioration in service is mostly related to the sulfation of the negative

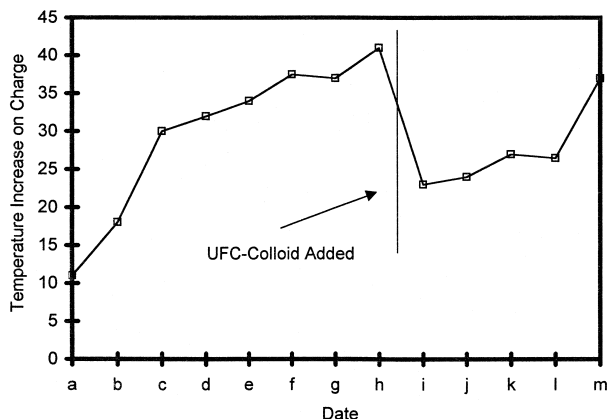


Fig. 5. Change in temperature during charge of an aircraft-engine starter battery. The same battery and reading dates as for Fig. 4.

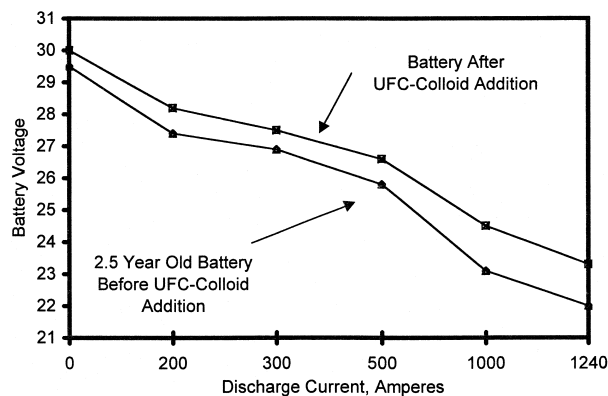


Fig. 6. Current–voltage curve for the aircraft-engine starter battery of Fig. 4, before and after adding UFC-colloid.

electrode. It is believed that sulfation occurs in these applications because of changes in the surface structure of the negative plate. The positive grid contains an antimony alloy for most batteries tested. During charge, grid corrosion results in antimony dissolution in the battery electrolyte. Repeated over-charge causes more antimony to dissolve into the electrolyte. The dissolved antimony will migrate to the negative electrode and deposit metallic antimony on the surface of the negative electrode. Antimony has a low hydrogen overvoltage and reduces the hydrogen overvoltage. This facilitates the evolution of hydrogen gas at the negative. Because of the low hydrogen overvoltage, water electrolysis takes place instead of the charge reaction whereby $PbSO_4$ converts to active lead. Therefore, $PbSO_4$ remains in the plate and the plate is said to be sulfated. This type of battery deterioration is seen in Figs. 4 and 5. The UFC-colloid additive is effective in correcting the sulfation. That the S.G. increases and the temperature is lower during charge (H through I in Fig. 5), after addition of the colloid, confirm this observation.

5. Results from fundamental research

The changes in the characteristics of the surface of a lead–lead sulfate ($Pb-PbSO_4$) electrode immersed in sulfuric acid were investigated with and without the UFC-colloid. The test electrode was a pure lead sheet on which $PbSO_4$ was deposited by anodic dissolution at 0.05 mA cm^{-2} for 3 h in 0.5 M H_2SO_4 . The electrodes were then transferred to 5.0 M H_2SO_4 (S.G. 1.280) and given 10 charge–discharge cycles with and without, UFC-colloid additions to the electrolyte. In these experiments, 5 vol.% of the UFC-colloid was added to the 5 M H_2SO_4 . SEM pictures of the electrode surface (both with and without UFC-colloid additive) were taken after charge and after discharge. Fig. 7a–d [4–6] show the structure of the

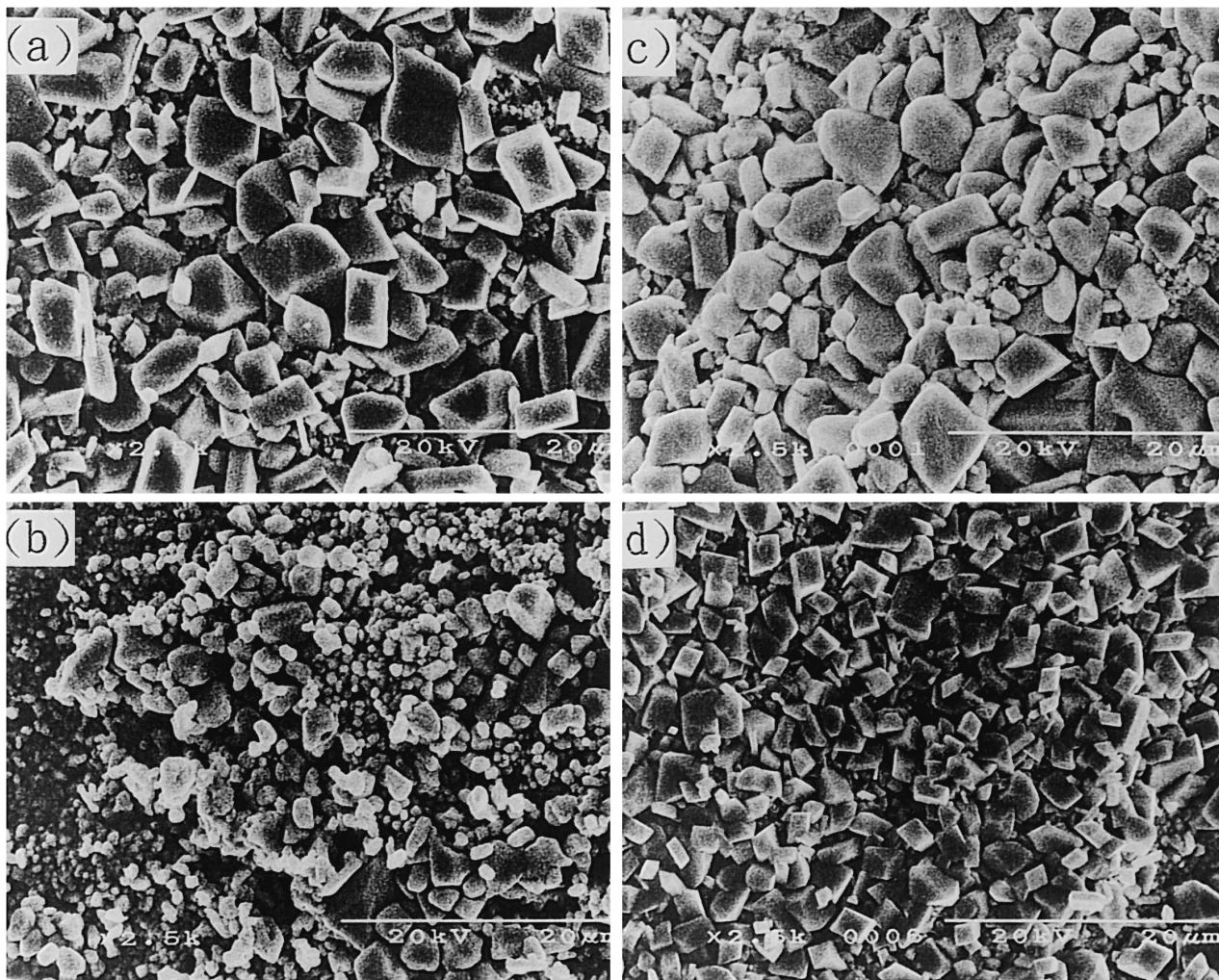


Fig. 7. SEM pictures of the lead negative electrode surface cycled 10 times in 5 M H_2SO_4 electrolyte. (a) Charged plate, no additive. (b) Charged plate, cycled with 5% by volume of UFC-colloid. (c) Discharged plate, no additive. (d) Discharged plate, cycled with 5% by volume of UFC-colloid.

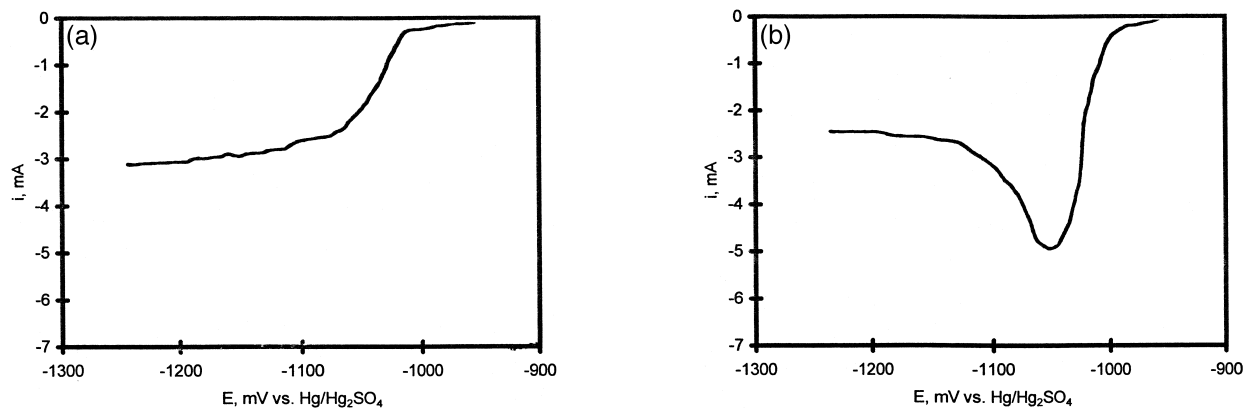


Fig. 8. Linear sweep voltammogram of a lead-lead sulfate electrode in 5 M H_2SO_4 at a sweep rate of 10 mV s^{-1} . Curve (A) without additive, curve (B) with UFC-colloid additive.

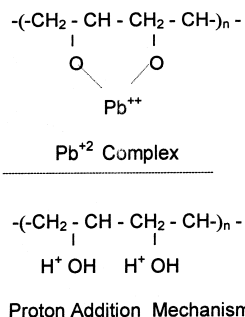


Fig. 9. Association of PVA molecules with H^+ and Pb^{+2} in acidic aqueous solution.

electrode surface for the various electrode conditions. In the presence of UFC-colloid additive, the size of the electrochemically produced lead crystals is much smaller as noted by comparing Fig. 7a and b. Also, the size of PbSO_4 crystallites produced upon discharge in the presence of UFC-colloid is much smaller than those formed without the additive. These results indicate that UFC-colloid can convert larger PbSO_4 into smaller size particles. This essentially returns the lead plate to the condition it was in at the beginning of service and indicates that the UFC-colloid is a good activator of a sulfated electrode.

In other experiments, the Pb-PbSO_4 electrodes were investigated by linear sweep voltammetry in 5.0 M H_2SO_4 (S.G. 1.280). Typical current–voltage curves, sweeping in the negative direction at a rate of 10 mV s^{-1} , are shown in Fig. 8a without the additive and in Fig. 8b with the UFC–PVA colloid. In the presence of the UFC-colloid, a much higher current peak was observed (Fig. 8b) than was observed without the UFC-colloid (Fig. 8a). An interpretation of these results can be based on the formation of a Pb^{+2} –PVA complex. The UFC–PVA colloid has a positive charge in the test electrolyte as confirmed by electrophoresis experiments. The positively charged PVA and

Pb^{+2} –PVA complex are depicted in Fig. 9. Electrodeposition of lead from the PVA-Pb^{+2} complex gives a much higher current peak than without any UFC-colloid additive. The complex seems to facilitate the lead electrode reactions. This is very reasonable in view of the electrochemistry of the lead complex [7].

6. Conclusion

UFC-colloid is effective to rejuvenate deteriorated lead–acid batteries with sulfation. The colloidal carbon adsorbs onto the sulfated plate and provides nucleation sites for deposition of lead during charge. It is also proposed that the formation of Pb^{+2} –PVA complex on the surface of the electrode plays an important role for the beneficial action. The practical test results of a large number of lead–acid batteries indicate that the UFC–PVA additive can significantly prolong the battery life.

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