



Short communication

Effect of additives on the performance of negative lead-acid battery electrodes during formation and partial state of charge operation[☆]

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ABSTRACT

Experiments were made with negative lead-acid battery electrodes doped with 1% of powdered carbon, titanium dioxide and silicone dioxide. It turned out that addition of carbon to the negative active mass causes an increase of the time of effective formation. During accelerated cycling in the PSoC regime, the electrode with carbon has in the course of the first PSoC run better properties than the electrode with titanium dioxide. The electrode with silicone dioxide performs the lowest cycle life. In the second PSoC run the electrode with carbon did not show a markedly better performance than the electrode with titanium dioxide. The positive effect of both carbon and titanium dioxide additives on the electrode cycle life is evident.

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1. Introduction

The favourable effect of powdered carbon on the performance of negative lead-acid battery electrodes has attracted the attention of many investigators [1–7]. A probable mechanism of the action of carbon in the negative lead-acid battery electrodes has been proposed in our preceding publications [1,2,8]. It has turned out that the effect of carbon is due to steric hindrance of the sulphate crystallization rather than the electric conductivity of graphite. Pavlov et al. [4] observed that the electrochemical reduction of lead sulphate on certain (electroactive) carbons proceeds at a lower overvoltage than on lead. The longest cumulative cycle life in accelerated PSoC tests can be attained at low graphite concentrations, apparently not exceeding 1% and the cycle life of the laboratory cells can be further increased by the application of external mechanical pressure [1].

2. Experimental

We employed six experimental electrodes of dimensions 55 mm × 20 mm × 7 mm with disconnected parallel ribs pasted with negative active mass prepared according to an industrial recipe with the exception that no carbon additive was used. With five electrodes, 1% (weight) of a special additive was added into each electrode active mass as shown in Table 1.

One electrode without additive served as a reference. Each negative electrode was combined with two positive electrodes (with an excess of active mass) and two 1.7 mm thick AGM separators of the type BG260 EB170 (H&V). The electrode packs were inserted into cells that could be hermetically closed, and finally filled with sulphuric acid of the density of 1.28 g cm⁻³. The electrode potential was measured against the cadmium reference electrode.

The cells were subjected to 23 formation cycles (consisting from 4 h charging at 0.2 A and 2 h stand). The effective rate of formation was characterized by the time necessary for a cell to exceed the voltage of 2.6 V and thus to enter the second charging stage.

After formation six conditioning cycles with voltage limitation were carried out in the flooded state. The cells were first discharged at the constant current of 0.7 A down to the final voltage of 1.6 V and subsequently charged at the constant current of 0.7 A with the voltage limit of 2.45 V for the period of about 20 h (one conditioning cycle per day). The courses of the cell voltage and potential of the negative electrode against time confirmed that the cell capacity is determined by the capacity of the negative electrode.

After conditioning cycles with voltage limitation, one conditioning cycle without voltage limitation was carried out. The end of charging was set as the moment when 110% of the withdrawn charge was supplied.

After experiments in flooded state, the excess electrolyte from the cells was drained off and the cells were hermetically closed. The cell capacity was then determined by one conditioning cycle. After adjusting to 50% state of charge, the cells were alternately charged and discharged at 2.5 A for 25 s and 3 s stand. Cycling continued until the voltage at the end of discharge dropped below 1.5 V.

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Table 1
Special additives to negative active masses.

Symbol	Manufacturer	Catalogue No.	Specific surface area (m ² g ⁻¹)	Grain size
SiO ₂ (nm)	Sigma-Aldrich	637238	140–180	10–20 nm
C (μm)	Graphite AG	CR2995	13	4 μm
C (nm)	Sigma-Aldrich	636835	40–300	5–10 nm
TiO ₂ (μm)	Lachema Neratovice	30444 0401	15	2–8 μm
TiO ₂ (nm)	Sigma-Aldrich	637226	200–220	<100 nm

The cell voltage was measured in every 100th charge/discharge half-cycle.

After the end of the first PSoC run, the electrodes were flooded; several conditioning cycles with voltage limitation and one conditioning cycle without voltage limitation were carried out. After finishing the record and adjusting to 50% state of charge, the second PSoC run was started.

3. Results and discussion

3.1. Formation

An overview of the results is given in Table 2.

During formation it can be seen from Table 2 that the electrode containing silicon dioxide was the first electrode that attained the second charging stage. During 10 h, however, the formation process could not be really finished; and since the cell voltage surpassed the gassing voltage, a further formation process was practically ineffective. In accord with the highest final cell voltage of 2.83 V, the electrode surface was visibly sulphated. Hence, the addition of silica, often used as gelling agent in accumulators, may be unfavourable for the negative active mass if it penetrates into the pores since it hinders effective formation.

Our present results confirm our recent finding [1] that the addition of carbon to the negative active mass causes an increase of the time of effective formation. Probably, the added material blocks some pores in the active mass thus interfering with the electrolyte transport. It is interesting that the time of formation seems to increase with the decreasing particle size of the additive (Table 2). Apparently, smaller particles may block the mass transport in the smaller pores which are more numerous.

During conditioning cycles, capacities of individual cells were measured. These are shown in Fig. 1. The capacity of an electrode with silicone dioxide additive [SiO₂ (nm)] is about one half to one third as compared with other electrodes, apparently because of the above-mentioned considerable degree of sulphation.

All electrodes exhibit a capacity increase after the first cycle, apparently due to the completion of formation of the remaining active mass particles. In the course of further conditioning cycles, the capacity of the additive-free electrode and of both electrodes containing TiO₂ (titanium dioxide) becomes gradually stabilized, whereas the capacity of both carbon-containing electrodes exhibits a downward trend.

Table 2
Evaluation of the formation rate.

Additive	Particle size	Time to complete formation (h)	Final voltage (V)
None	–	22	2.826
SiO ₂	10–20 nm	10	2.830
C (μm)	4 μm	40	2.749
C (nm)	5–10 nm	58	2.619
TiO ₂ (μm)	2–8 μm	40	2.787
TiO ₂ (nm)	<100 nm	64	2.788

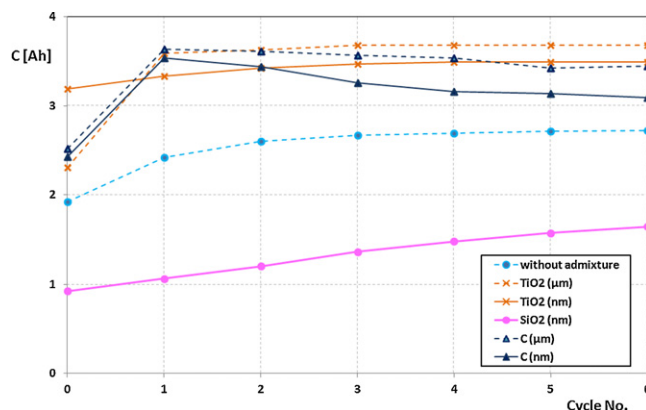


Fig. 1. Evolution of cell capacities during conditioning cycling.

3.2. Conditioning cycling

Fig. 2 shows the charging curves of the individual negative electrodes in the flooded regime without voltage limitation. Results show that the charging curves of individual negative electrodes display two charge stages. The potentials of individual negative electrodes increase slowly with time during the first stage and then become virtually unchanged during the second stage. There are sensible differences in the rate of attaining the second stage. The electrodes with silica and without additive attained the second stage earlier, namely at the 60% and 65% state of charge, respectively. Electrodes with TiO₂ and carbon attained the second stage later, namely at 75% and 84% state of charge, respectively. This means that their charge acceptance was much better. The course of the potential of the negative electrode corresponds to the course of the cell voltage, hence the potential of the positive electrodes can be considered constant.

Fig. 3 shows the change in negative-plate potential during charging after removing the excess electrolyte and hermetically sealing the cells. It can be seen that the attainment of the second charging stage has been still more shifted, namely with the electrodes containing TiO₂ and carbon toward 85 and 95%, respectively.

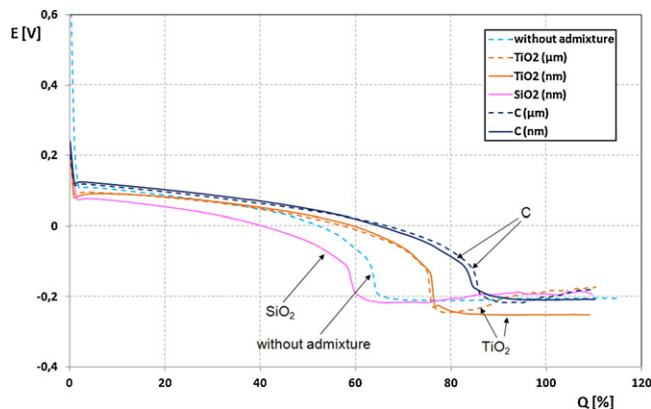


Fig. 2. Potential of negative electrode during charging in flooded regime.

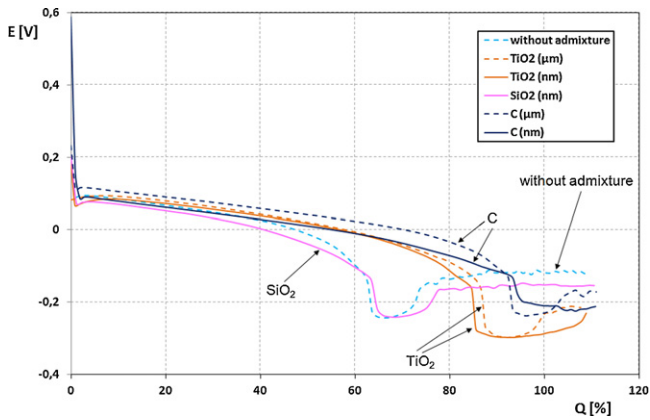


Fig. 3. Potential of negative electrode during charging in the hermetic regime.

This shift is caused by the starting reduction of oxygen coming from the positive electrode. An alternative reason could be that the negative plates were oxidized by exposure to atmospheric oxygen, in the period between the removal of surplus electrolyte and the subsequent hermetic sealing of the cells. But the whole time the negative active mass was fully covered by AGM separator soaked with electrolyte and that is why this explanation (oxidizing by exposure to atmospheric oxygen) is not probable. However, at the end of charge, as soon as the pressurized oxygen finds its way through the separator pores, the potential of the negative electrode is shifted by 80–100 mV back to less negative values.

3.3. Accelerated PSoC cycling

Change in end-of-charge voltage during the first PSoC run is shown in Fig. 4. The initial cell voltage ranges between 2.26 and 2.30 V for the electrodes with carbon or TiO₂ and is equal to 2.39 V for the electrode with the SiO₂ additive. It was just this electrode that very quickly attained the maximum voltage which grew nearly to 3.1 V. This fact shows a considerable internal resistance of the cell. The cycle life of the additive-free electrode was about 20,000 cycles; the final voltage was almost equal to 3 V. Both electrodes with the TiO₂ additive attain in the course of charging the voltage of 2.60 V (Fig. 4) and then exhibit a very slow steady decrease. The voltages of the electrodes with carbon additive are somewhat lower. The course of the cell voltage corresponds to the course of the potential of the negative electrode.

Change in end-of-discharge voltage during the first PSoC run is shown in Fig. 5. The shortest cycle life was recorded for the electrode with the SiO₂ (nm) additive, namely 3300 cycles; this

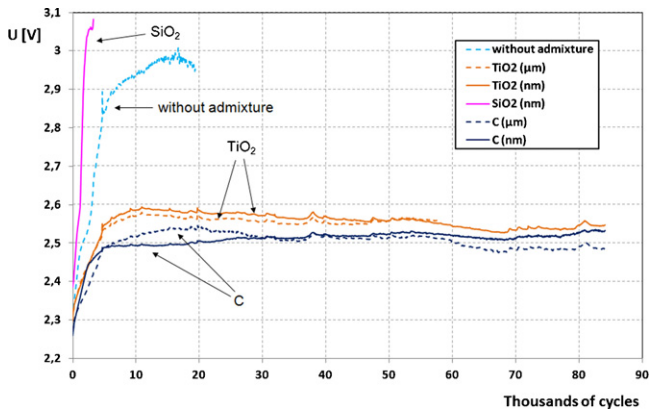


Fig. 4. Voltage at the end of charging as a function of the number of cycles, 1st PSoC run.

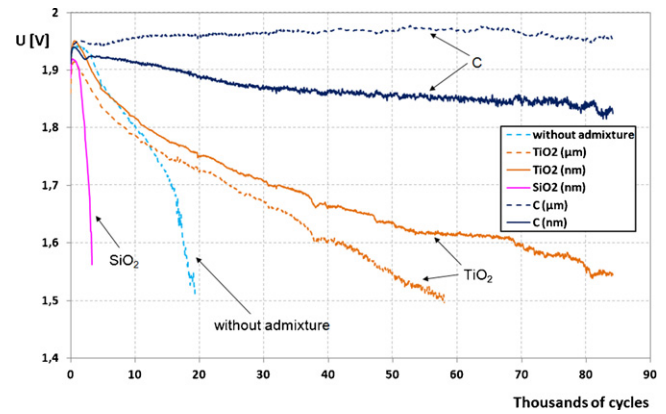


Fig. 5. Voltage at the end of discharging as a function of the number of cycles, 1st PSoC run.

electrode also featured the steepest voltage drop. The cycling life of the additive-free electrode was 19,400 cycles. The cycle life of the electrode with TiO₂ (μm) attained 58,300 cycles. Neither of the two electrodes containing carbon nor the electrode with the TiO₂ (nm) additive attained (within 85,000 cycles) the end voltage limit of 1.5 V. The course of the cell voltage corresponds to the course of the potential of the negative electrode.

The positive effect of carbon and titanium-dioxide additives on the cycle life of the electrodes is evident. The electrode with carbon has in the course of the first PSoC run better properties than the electrode with TiO₂.

Fig. 6 shows the charging curves of the individual negative electrodes in the flooded regime without voltage limitation after the end of the first PSoC run. Results show that some changes have been observed with the second charging stage. The electrode with the SiO₂ (nm) additive reaches the second charging stage at 74%, which means an improvement by 14% compared to Fig. 2. This can be understood since the sulphate is gradually removed from the electrode, as confirmed by a continuous moderate growth of capacity and decrease of the active mass resistance over the course of the whole cycling life of the electrode.

The additive-free electrode proceeds to the second charging stage at 77% of the charge supplied (improvement by 12%). Both electrodes with the TiO₂ additive proceed to the second charging stage at 82–84% of the charge supplied (improvement by about 8%) and both electrodes with the carbon additive at 82–85% (no improvement, as these electrodes were close to their performance limit).

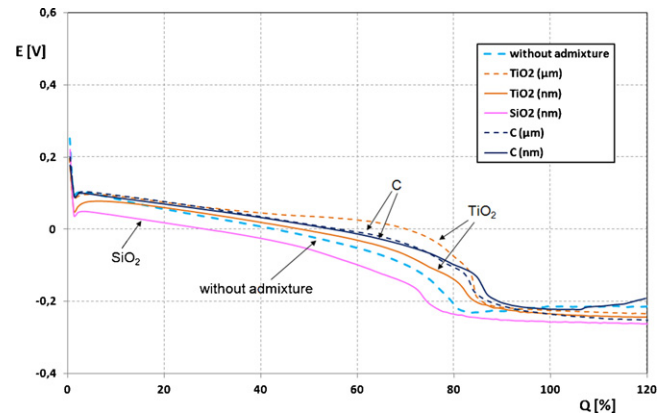


Fig. 6. Potential of negative electrode during charging in flooded regime after 1st PSoC run.

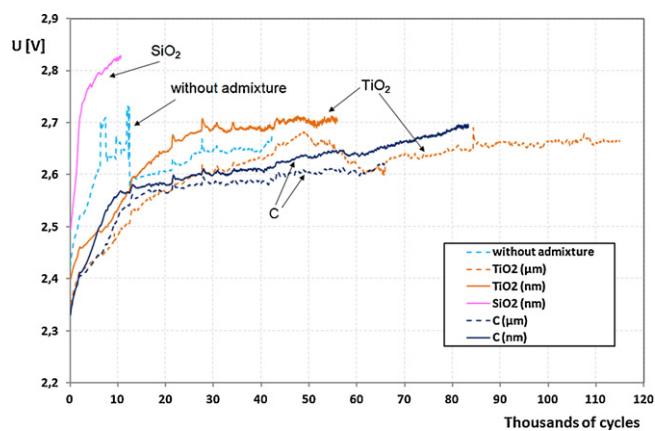


Fig. 7. Voltage at the end of charging as a function of the number of cycles, 2nd PSoC run.

Change in end-of-charge voltage during the second PSoC run is shown in Fig. 7. The initial cell voltage (Fig. 7) was in the 2.33–2.40 V range for electrodes with carbon and TiO₂ additives; 2.43 V for the additive-free electrode, and 2.50 V for that with the SiO₂ additive. These values were for all electrodes by 70–100 mV higher than with the first PSoC run, evidence for an increase of the internal cell resistances.

The electrodes with SiO₂ or without additive again attained the highest voltages which, nevertheless, were by about 280 mV lower than those in the first PSoC run (Fig. 4). This seems to be related to the marked improvement of the performance of these two electrodes. The cycle life also improved; the electrode with the SiO₂ additive reached 10,000 cycles and the reference additive-free electrode attained about 42,000 cycles.

The final voltage for electrodes doped with carbon or TiO₂ was by about 50–100 mV higher than that in the first PSoC run which again points to an increase of the internal resistance of the cells during PSoC runs. The moment when the voltage was highest was, in comparison with the first PSoC run, delayed and did not exhibit a downward trend. The course of the cell voltage corresponds to the course of the potential of the negative electrode.

Change in end-of-discharge voltage during the second PSoC run is shown in Fig. 8. The electrode with the SiO₂ additive exhibited the shortest cycling life of 10,500 cycles (in the first PSoC run 3300 cycles). The cycle life of the additive-free electrode was 42,000 cycles (in the first PSoC run 19,400 cycles). The electrodes with both carbon additives as well as the electrode with TiO₂ attained in the

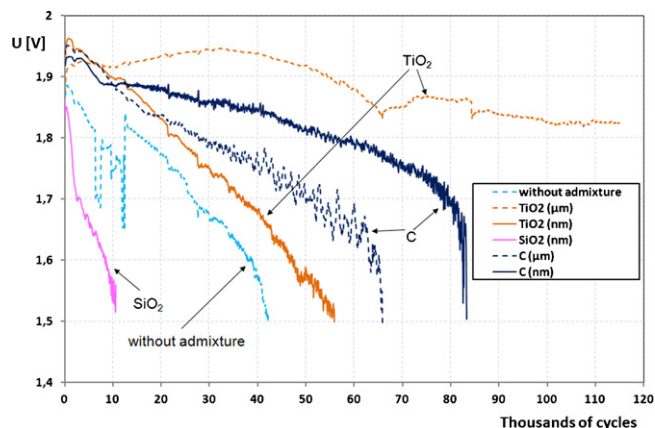


Fig. 8. Voltage at the end of discharging as a function of the number of cycles, 2nd PSoC run.

Table 3
Comparison of cycle lives for electrodes in the first and second run.

Additive	Cycle life in 1st run	Cycle life in 2nd run
None	19,400	42,000
SiO ₂	3300	10,500
C (μm)	>90,000	65,800
C (nm)	>90,000	83,300
TiO ₂ (μm)	58,300	>120,000
TiO ₂ (nm)	~90,000	58,200

second PSoC run worse results than in the first PSoC run. The cycle life of the electrode with the TiO₂ (nm) additive was 58,200 cycles (in the first PSoC run 90,000 cycles by extrapolation). The electrodes with C (μm) and C (nm) additives featured the most marked loss of the cycle life attaining 65,800 and 83,300 cycles, respectively, whereas in the course of the first PSoC run they even did not attain the end of their cycle life.

It was only the electrode with the TiO₂ (μm) additive which exhibited in the second PSoC run a better performance and which by the end of the second PSoC run (120,000 cycles) did not reach the voltage limit of 1.5 V (it reached 58,300 cycle in the first PSoC run).

The positive effect of both carbon and titanium dioxide additives on the electrode cycle life is evident, although in the second PSoC run the electrode with carbon did not show a markedly better performance than the electrode with TiO₂. The results shown in Fig. 8 are surprisingly more favourable for titanium dioxide than for carbon.

A summary of all cycling results is shown in Table 3. It seems that the cycle life of the electrodes shows some correlation with the rate of attainment of the second charging step (cf. Table 2), but more measurements would be necessary.

4. Conclusions

Addition of carbon to the negative active mass causes an increase of the time of effective formation. The electrode with carbon has in the course of the first PSoC run better properties than the electrode with TiO₂. The electrode with SiO₂ performs the lowest cycle life. In the second PSoC run the electrode with carbon did not show a markedly better performance than the electrode with TiO₂. The positive effect of both carbon and titanium dioxide additives on the electrode cycle life is evident.

During charge in the PSoC mode, an important role is played by the additive (C and TiO₂), which lowers the final voltage of the cell and at the same time reduces the magnitude of pores in the negative electrode. These mechanisms improve the ability of electrode to accept large charging currents and limit the growth of sulphate crystals.

In case of discharge at high currents in the PSoC mode, a significant role is played by the internal cell resistance, which brings about an initial voltage drop and affects the resulting cycling life of the electrode.

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