

Influence of phenolic group content in lignin expanders on the performance of negative lead–acid battery plates

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Abstract

Negative plates for lead–acid batteries containing lignin expander UP-414 with various phenolic group contents have been investigated. The members of the family of lignins UP-414 are produced by Borregaard LignoTech, Norway and differ mainly by the amount of phenolic groups and less so by the carboxylic groups in their structure, the content of all other functional groups (methoxyl, ketonic, etc.) being the same for all UP-414 products. The influence of phenolic group content in the expander on the performance of SLI batteries has been studied. It has been established that the batteries with PbSb grids exhibit a decline in C_{20} capacity, CCA performance and cycle life, when the content of phenolic groups in the expander increases. The capacity, cycle life and self-discharge of batteries with PbSnCa grids do not depend on the content of phenolic groups in the lignin. It has been proved experimentally that lignin reacts with the ions of the grid alloying additives forming metal–lignin compounds, which exert an influence on the performance of the negative plates.

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Keywords: Lead–acid battery; Expanders; Lignins; Phenolic groups in lignin; Metal–lignin compounds

1. Introduction

Organic expanders based on lignins exert an influence on the processes of charge and discharge of negative lead–acid battery plates. Being surface active substances, they also affect the hydrogen overvoltage on the negative electrode. This influence of the expander is mainly due to the functional groups in its structure: methoxy, phenolic, carboxyl, ketonic, carbinol structural groups, etc., which affect the above processes and thus the performance of the battery. Lignins and their derivatives present polymer substances with a fairly complex structure comprising, a great variety of functional groups, and the different functional groups occupy a variety of positions in the polymer structure of the expander. Moreover, the active functional groups affect, via different mechanisms, the crystallisation, the physico-chemical and electrochemical processes during formation and the degradation of the negative active mass on charge and discharge. The influence of a given functional group on the performance characteristics of the negative plates is thus very complex and also depends on the influence of the other functional groups. Moreover, the expander is subjected to

oxygen attack by the oxygen evolved on the positive plate and also to hydrogen attack by the hydrogen evolved on the negative plate [1]. Hence, the chemical stability of the expander is important for the cycle life of the battery.

In a previous paper of ours, we studied the effect of the functional groups contained in a family of eight lignin products on the performance of SLI batteries when tested according to the DIN-43539-2 standard [2]. It was established that phenolic-OH groups (Ar-OH) and the purity of the lignins, expressed by K_{solid} exert an influence on most of the battery parameters. The effect of phenolic groups on battery performance has been investigated earlier [3,4]. It has been found that phenolic groups have a beneficial effect on the behaviour of the negative plates. A second hydroxyl group in the structure of the phenol nucleus improves the performance of the negative plate in ascending order depending on the position it occupies, i.e. *ortho*, *meta* or *para*. The influence of phenolic groups can be determined unambiguously if a series of expanders is produced with similar functional group composition, varying only in the phenolic group content. Such a series of lignin products, UP-414, with six different contents of phenolic groups, was manufactured by Borregaard LignoTech (Norway).

The aim of the present paper is to investigate the influence of the phenolic group content in the lignin on the performance of SLI batteries.

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2. Experimental

2.1. Expanders

The content of phenolic groups in the individual members of the UP-414 family of expanders is presented in Table 1.

The phenolic hydroxyl was blocked by a reaction with dimethyl sulphate (DMS) at high pH. However, DMS reacts rapidly with carboxylic acids as well. As a result of these reactions, the samples of UP-414 with 0.28 and 0.60% Ar-OH, i.e. with the lowest amounts of Ar-OH, contain no, or very low amount of, carboxylic acid. The lignin UP-414 with 2.02% Ar-OH was not treated with DMS and it contained approximately 5% carboxylic acid. As a result of the above reaction, the contents of phenolic and carboxyl groups were changed in the UP-414 family of expanders.

2.2. Negative plates

The negative plates used in this investigation were produced using lead oxide LO (75% degree of oxidation). The paste was prepared with $H_2SO_4/LO = 4.5\%$, 0.4% lignin, 0.8% $BaSO_4$ and 0.2% carbon black. Two types of commercial SLI grids were used: low-antimony (Pb–1.8%Sb–0.1%As–0.2%Sn) and lead–calcium (Pb–0.3%Sn–0.06%Ca) ones. The plates were set to curing and formation employing standard technologies.

2.3. Batteries

Batteries (12 V/38 A h) were assembled with four negative and five positive plates per cell. The batteries were of the flooded type with polyethylene separators (Daramic-Daga) and H_2SO_4 with sg 1.28. The performance of the batteries was limited by the negative plates and their potential was measured in all tests.

2.4. Battery tests

All batteries were cycled according to the DIN-43539-2 test protocol for SLI batteries. Two batteries with each type of expander were tested, one to determine the initial performance characteristics (three initial C_{20} capacity tests and two CCA tests) and the cycle life, and the second one to measure the charge acceptance and self-discharge performance. The utilisation of the negative active mass during the initial capacity and CCA tests was 50%. A detailed description of the battery test procedure is given in [2].

Table 1
Content of phenolic groups in the expanders of the UP-414 family of lignin products

Content of phenolic-OH groups (wt.%)	2.02	1.72	1.21	1.04	0.60	0.28
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3. Experimental results and discussion

3.1. C_{20} capacity tests

Fig. 1 presents the results of the three initial C_{20} capacity tests versus the phenolic group content in the expander for batteries with PbSb grids (Fig. 1a) and PbSnCa grids (Fig. 1b). With increase of the content of Ar-OH groups in the expander the C_{20} capacity of batteries with PbSb grids tends to decrease. Each subsequent capacity test gave a lower value as compared to the preceding one, the greatest difference being observed between the first and the second tests.

The capacity of the batteries with PbSnCa grids exhibit a pronounced tendency to decline during the first discharge with increase of the content of Ar-OH in the expander. During the second discharge, the capacity values are lower than those of the first cycle. This decrease is most pronounced at low Ar-OH concentrations (0.25, 0.6%). During the third cycle, the capacity increases slightly as compared to the second cycle. It can be presumed that during the two initial deep discharge cycles the Sn ions dissolved in the H_2SO_4 solution react with the expander and the metal–organic compound obtained reaches such quantities that have a positive effect on the capacity during the third cycle.

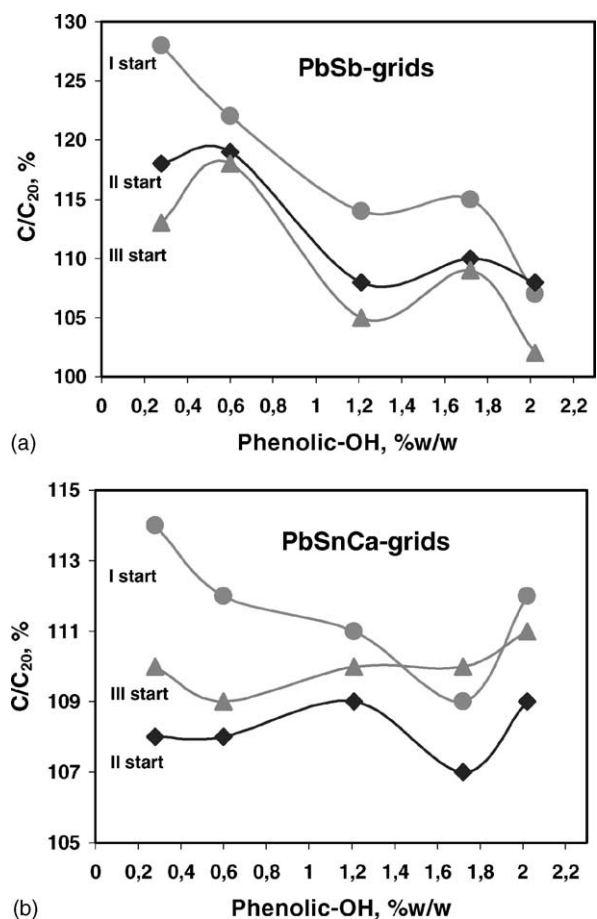


Fig. 1. Initial C_{20} capacity vs. phenolic group content in the lignin. C_{20} is the rated capacity at 50% NAM utilisation.

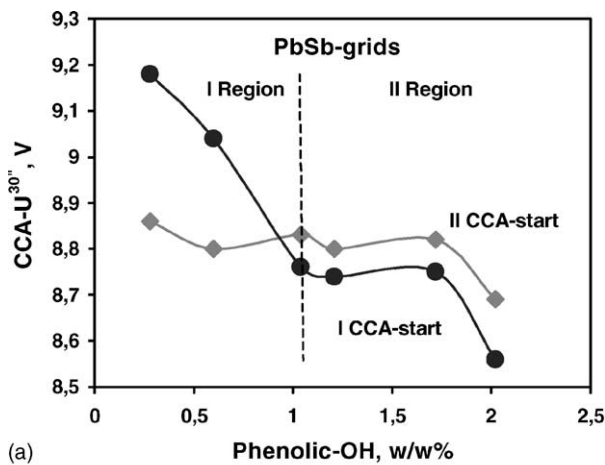
At phenolic content below 1.0%, the initial C_{20} capacity of the batteries with PbSb grids is higher by about 10% than that of the batteries with PbSnCa grids. When the phenolic group content is greater than 1.0%, the C_{20} capacity values are almost equal for all batteries, irrespective of grid type, with a minimum advantage of the batteries with PbSnCa grids.

3.2. Cold cranking ability tests

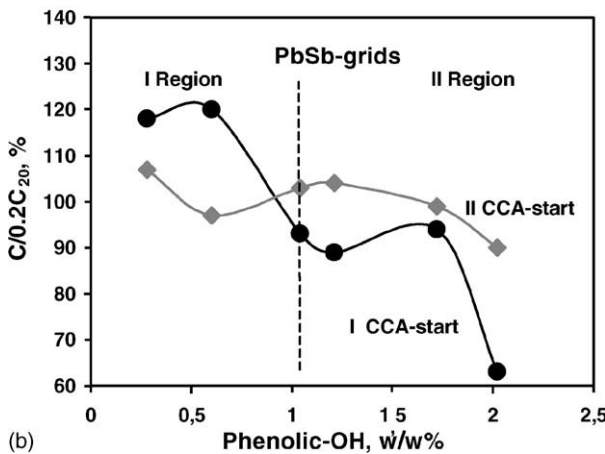
Following the requirements of the DIN-43539-2 standard, we performed two CCA discharge tests with discharge current $I = 5C_{20}$ at $t = -18^\circ\text{C}$. The voltage at the 30th second and the capacity versus 0.2% of the rated C_{20} value were measured. Fig. 2 presents the results obtained for batteries with PbSb grids. During the first CCA test, two regions are observed: the $U_{30''}$ value decreases for batteries with low phenolic group content (region I) and it remains almost constant for their high phenolic content counterparts (region II). During the second CCA test, $U_{30''}$ depends but slightly on the content of phenolic groups in the expander. Fig. 2b shows the CCA capacity as a function of phenolic content in the lignin. It can be seen that during the first CCA

test, the capacity decreases with increase of the phenolic content, whereas during the second test, the capacity depends but slightly on the phenolic group content.

The dependencies of $U_{30''}$ and CCA capacity on the content of phenolic groups in the expander for batteries with PbSnCa grids are presented in Fig. 3. It is evident from Fig. 3a that during the first CCA test the $U_{30''}$ values tend to increase with increase of the phenolic content. During the second test, the curves feature two regions and the influence of the content of phenolic groups is fairly complicated, which might be due to the formation of various metal–organic compounds with different impact on this parameter. Another reason for the formation of these two regions can be the content of carboxyl groups in the lignin. It is low in the samples with phenolic group content up to 1.0% and increases substantially in the samples with higher phenolic content. The increased carboxylic amount improves the CCA performance [2]. Fig. 3b evidences this tendency of the cold cranking capacity. On comparing Figs. 2a and 3a it can be seen that the batteries with PbSnCa grids exhibit higher $U_{30''}$ values than those with PbSb grids. Fig. 3b shows the CCA capacity versus phenolic group content dependence. Two regions are observed. In the phenolic content

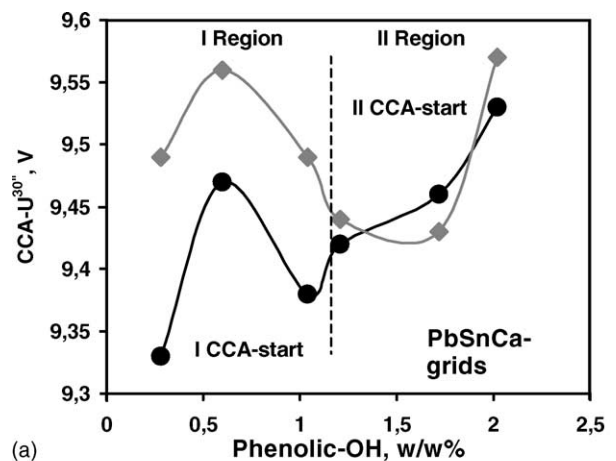


(a)

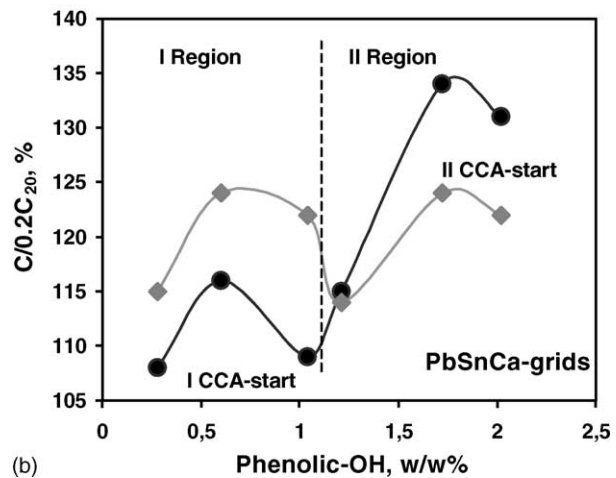


(b)

Fig. 2. Initial CCA test: $U_{30''}$ and C_{CCA} vs. phenolic content in the lignin for batteries with PbSb grids.



(a)



(b)

Fig. 3. Initial CCA test: $U_{30''}$ and C_{CCA} vs. phenolic content in the lignin for batteries with PbSnCa grids.

region above 1.20%, during the first CCA test the capacity at $-18\text{ }^{\circ}\text{C}$ increases. A tendency to levelling the CCA capacities of the batteries is observed during the second CCA test.

The above discussed changes in expander activity support the presumed interaction between the lead, antimony and tin ions of the grid alloy with the phenolic groups contained in the expander.

3.3. Cycle life test

The test was performed at $40\text{ }^{\circ}\text{C}$. One week-cycle comprised 10 charge–discharge cycles. The end-of-discharge

voltage at the 10th cycles was measured. The battery was left on open circuit for 65 h at $40\text{ }^{\circ}\text{C}$ and after that a CCA test was performed. Fig. 4 presents the end-of-discharge voltage at the 10th week-cycle as a function of the number of weeks. Fig. 5 shows the dependencies of the number of week-cycles (giving the cycle life of the battery) on the content of phenolic groups in the lignin for both types of batteries under test. Judged by this parameter (with an end-of-life limit $U_{10\text{ cycle}} = 10\text{ V}$), the cycle life of the batteries depends on the type of grid alloy used and on the phenolic group content in the expander. The batteries with PbSb grids improved their cycle life performance with increase in the

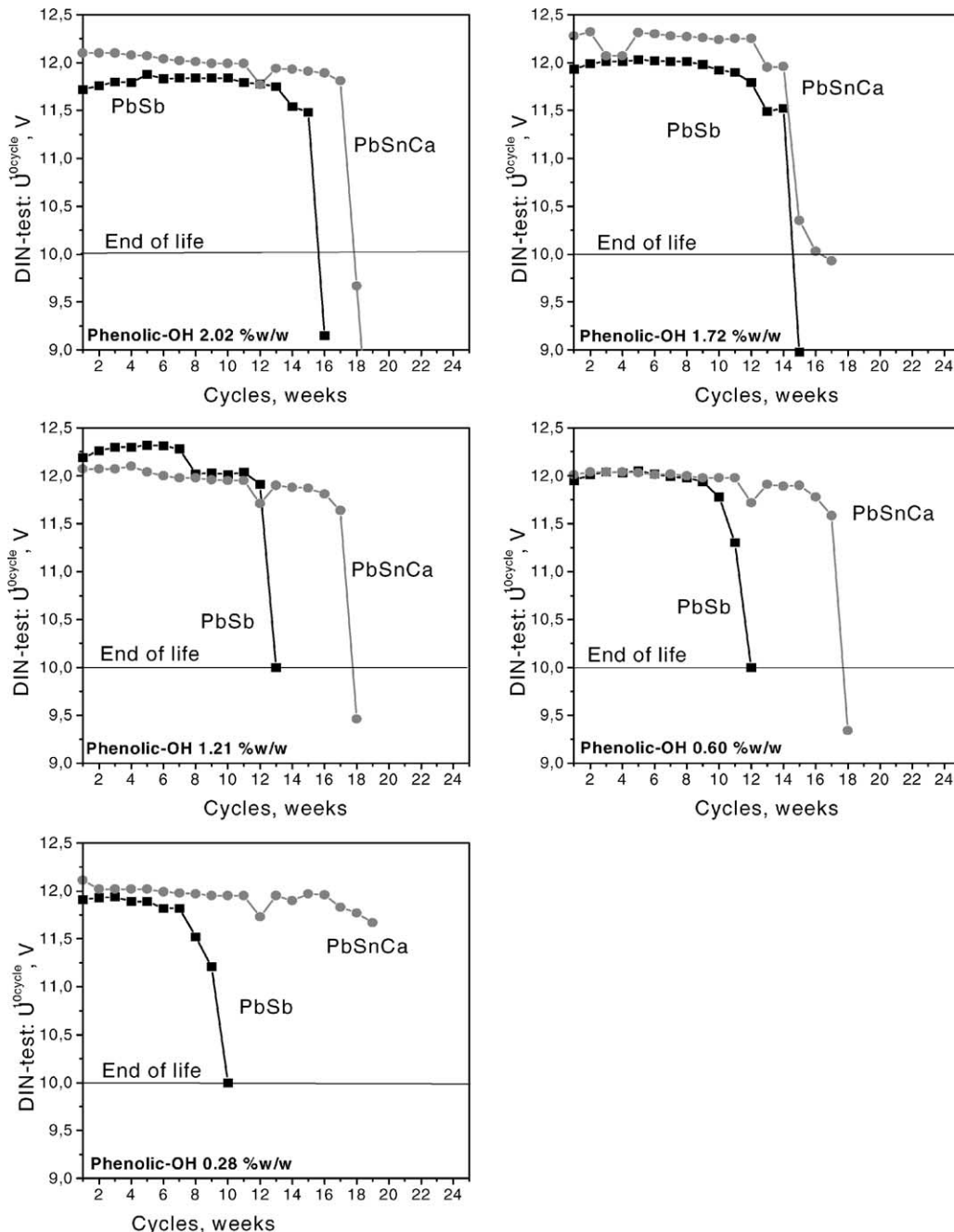


Fig. 4. DIN cycle life test results: $U_{10\text{ cycle}}$ voltage as a function of the number of week-cycles for batteries with PbSb and PbSnCa grids.

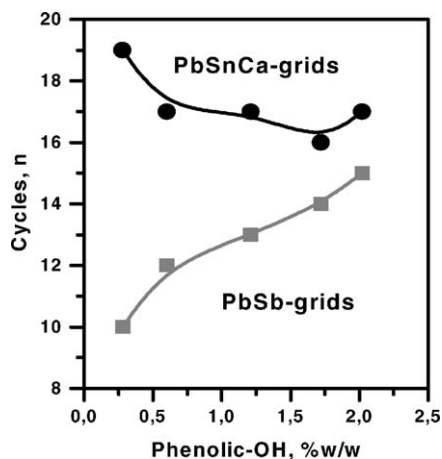


Fig. 5. Cycle life as determined by the voltage at the 10th week-cycle vs. phenolic-OH content in the lignin.

content of phenolic groups, whereas the life of batteries with PbSnCa grids decreased slightly.

Fig. 6 presents the voltage at the 30th second of the CCA test measured at the end of each week-cycle versus the number of week-cycles. Fig. 7 shows the dependencies of the $U_{30''}$ voltage during the CCA test at the 10th week-cycle as a function of the phenolic group content in the expander. The $U_{30''}$ values for the batteries with PbSb grids are lower than those for their PbSnCa counterparts. With increase of the phenolic content the $U_{30''}$ voltage decreases for the batteries with PbSb grids and remains almost unchanged for the PbSnCa batteries.

Fig. 8 presents the number of cycles until 70% of the $0.2C_{20}$ capacity is reached during the CCA test versus the content of phenolic groups in the expander. The latter does not affect the cycle life of the batteries with PbSnCa grids, which is 14 ± 1 weeks. The batteries with PbSb grids have shorter cycle life, which decreases with increase of the phenolic group content passing through a minimum at 1.7% phenolic-OH. The apparent increase of the life of the battery with 2.02% phenolic-OH content could be due to higher concentration of the carboxylic acid in the lignin. One possible reason for the shorter cycle life of the batteries with PbSb grids versus those with PbSnCa ones may be the accelerated self-discharge processes on the negative plates during the 65-h open circuit stay of the battery at 40 °C. The plates with PbSnCa grids suffer much slower self-discharge.

3.4. Charge acceptance and self-discharge tests

According to the requirements of the DIN standard, these tests are conducted with batteries that have undergone only initial performance tests: three C_{20} capacity measurements and two CCA tests. The batteries were discharged with $I = 2I_{20}$ at 25 °C down to $DOD = 0.5C_{20}$ A h, then left on open circuit at 0 °C for 18 h. The charge acceptance was determined on charging of the batteries at 14.4 V, the

current being measured at the 10th minute. To meet the requirements of the DIN standard, this current should be higher than $4.0I_{20}$ A, where I_{20} is the current at 20-h rate of discharge. Fig. 9 compares the current measured at the 10th minute versus the DIN required value as a function of the phenolic group content in the expander. The batteries with PbSb grids have higher charge acceptance than the required value and it increases with increase of the phenolic content. The charge acceptance of the batteries with PbSnCa grids is close to the value required by the DIN standard and a tendency to slight increase with increase of the phenolic content is observed.

When studying the effect of phenolic groups contained in the different types of lignins, it has been found that they reduce the charge acceptance of the plates [2]. In the case of UP-414 expander with varying phenolic group content, the higher phenolic-OH content causes a slight increase in charge acceptance (Fig. 9). This contradiction between the experimental data for the two families of lignins is probably a result of the influence of other functional groups in the lignin structure [2]. In this particular case [2], the effect of the other functional groups is stronger than that of phenolic groups and hence they have a dominating role in determining the charge acceptance of the battery. For the UP-414 family of expanders only the carboxylic and the phenolic groups influence the charge acceptance of the battery.

The next test to which the batteries were set was the self-discharge test. Charged batteries of the two types were left on open circuit for 21 days at 40 °C. Then a CCA test was conducted. Fig. 10 shows the obtained CCA capacity versus phenolic content curves.

A notable self-discharge is observed with the batteries with PbSb grids and it increases with increase of the phenolic group content. A similar dependence was also noted when studying the effect of phenolic content in various types of lignins on the self-discharge of PbSb batteries [2]. It can be assumed that the rate of self-discharge is more markedly affected by the content of phenolic groups if the negative plates are produced with PbSb grids. The batteries with PbSnCa grids exhibit slow self-discharge which is almost independent of the phenolic content in the expander (Fig. 10). The only exception is the battery with expander containing 2.02% phenolic groups, but this expander contains more carboxylic acid groups as well.

3.5. Specific surface of the negative (Pb) active mass before and after the DIN cycle life test

Fig. 11 presents the specific surface area of charged NAM, before and after cycling, as a function of the phenolic group content. The NAM surface for both types of plates, with PbSb and PbSnCa grids, decreases on cycling. Before cycling, the NAM surface of PbSb plates is greater than that of PbSnCa ones. It is evident from the data in Fig. 11 that, except for the plates with 2.02% phenolic content and

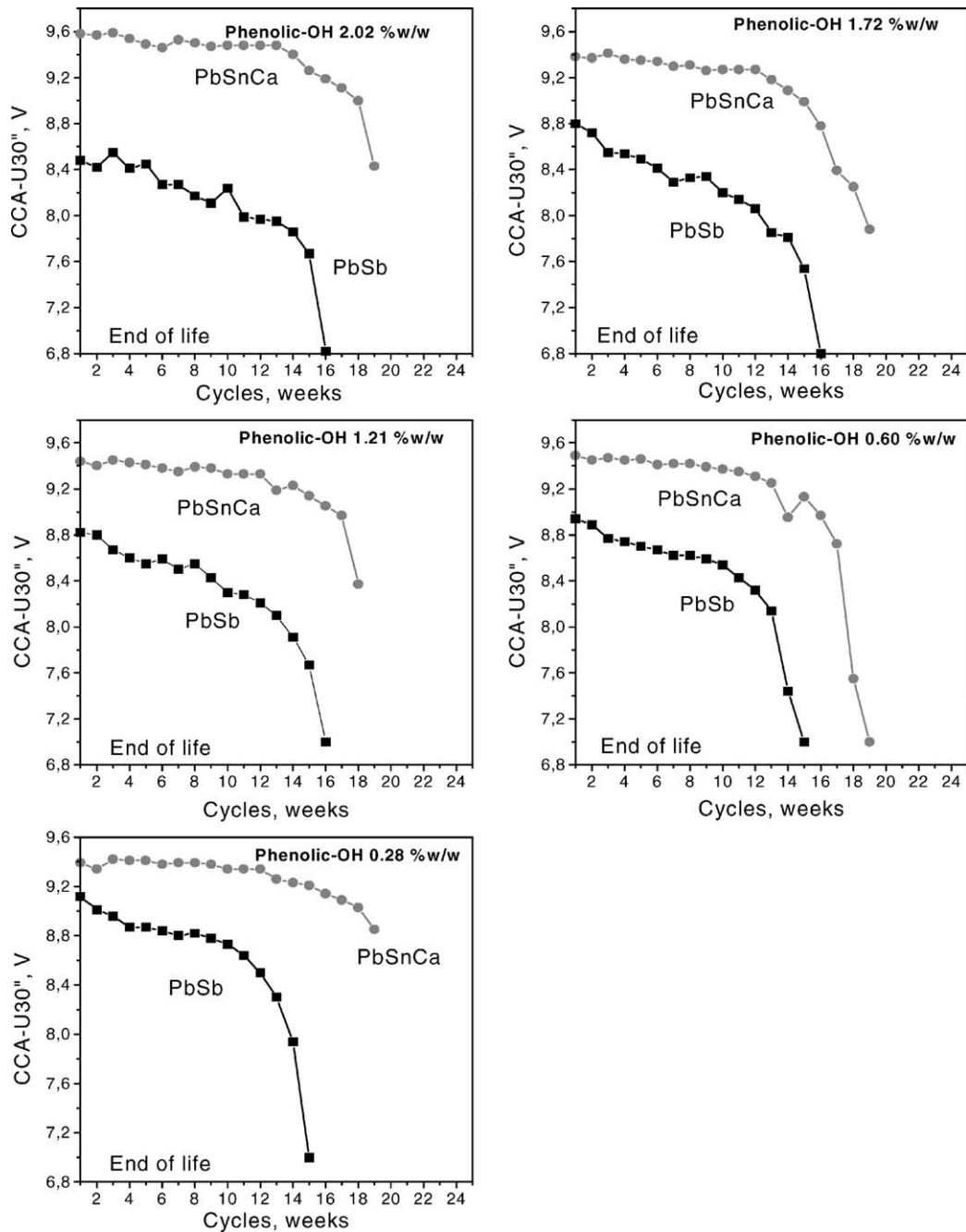


Fig. 6. U_{30v} during the CCA test vs. the number of week-cycles for batteries with different phenolic-OH content in the lignin.

higher carboxylic acid concentration in the lignin, the phenolic-OH content does not affect substantially the specific NAM surface. This means that the changes in phenolic content do not influence the size of the lead particles building up the negative active mass.

3.6. SEM examinations of NAM before and after the cycle life test

Fig. 12 shows SEM micrographs of charged NAM formed on PbSnCa negative plates with 0.28 wt.% phenolic group

content in the expander, before and after the cycle life test. During formation of the negative plates, the negative active mass obtained comprises skeleton and small lead crystals deposited onto it. These crystals are involved in the charge-discharge processes and they are called “energetic structure” [5]. An analogous picture is observed in Fig. 12a. The size of the small crystals is between 0.8 and 2 μm and these give a relatively large NAM surface. It can be seen from Fig. 12b that after cycling, the NAM consists of lead particles sized between 2.5 and 5 μm . These particles have smooth surface and their structure looks very much like that

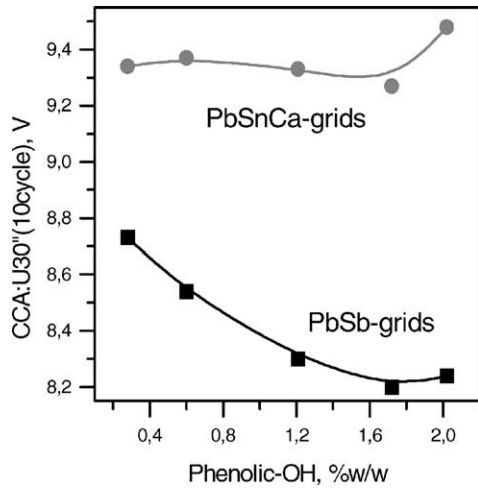


Fig. 7. U_{30v} during the CCA test after every week-cycle vs. phenolic group content in the lignin.

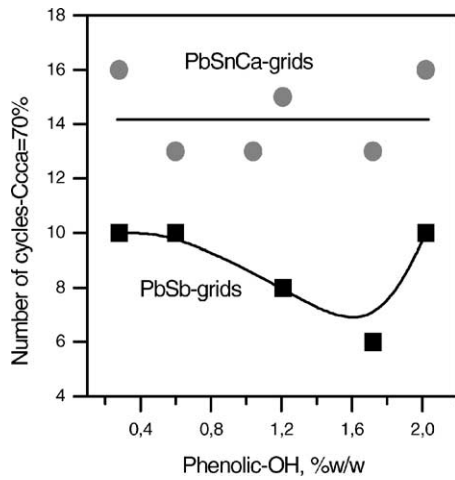


Fig. 8. Battery cycle life as determined by the CCA capacity vs. phenolic-OH content.

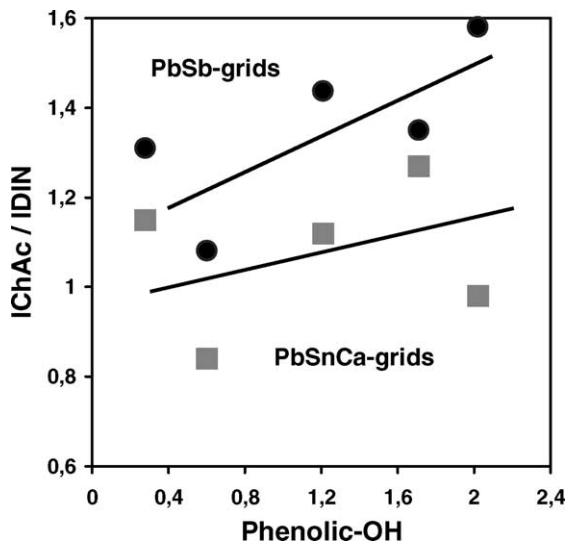


Fig. 9. Charge acceptance test. Current at the 10th minute vs. the DIN required value as a function of phenolic group content in the expander.

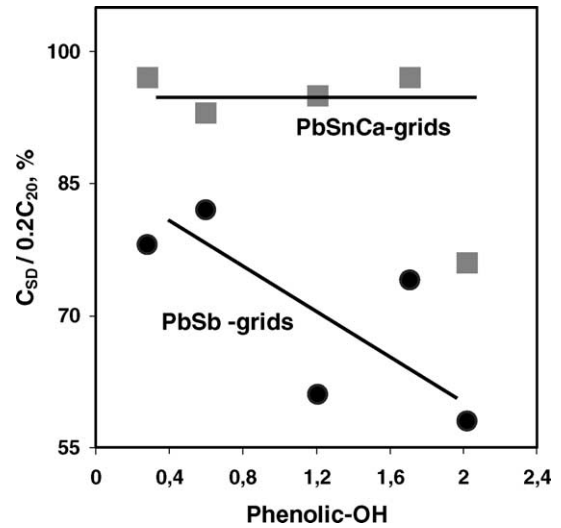


Fig. 10. Self-discharge test. CCA capacity vs. the DIN required value as a function of phenolic group content in the expander.

of the skeleton. Only a small number of Pb nuclei are distinguished on the skeleton. The NAM surface here is small. Hence, it can be concluded that during cycling the “energetic structure” of NAM is converted into skeleton

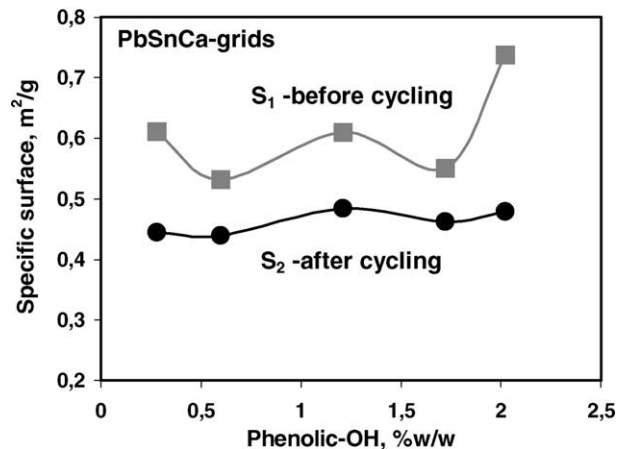
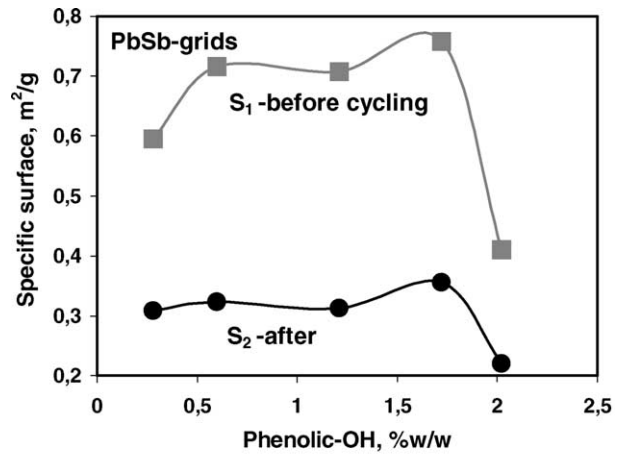


Fig. 11. Specific surface of NAM before and after cycling.

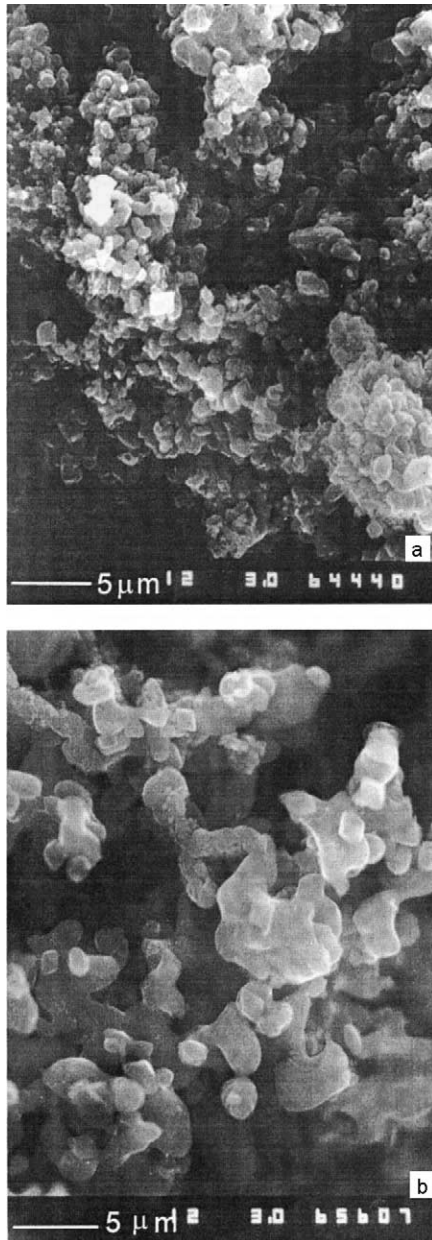


Fig. 12. SEM analysis of PbSnCa negative plate (0.28 wt.% phenolic-OH group content in the lignin): (a) charged NAM before cycling; (b) charged NAM after cycling.

one, the NAM surface decreases and so does the capacity of the plate.

The structure of NAM with 1.70 wt.% phenolic group content in the expander, which is presented in Fig. 13 is analogous to the one shown in Fig. 12.

Figs. 14 and 15 present SEM micrographs of the NAM of plates with PbSb grids before and after cycling. Similar phenomena to the ones discussed above (for the PbSnCa grids) proceed on these plates. The pictures in Figs. 12–15 indicate that at the end of battery life, the NAM skeleton is involved in the charge and discharge processes. The energetic structure has disappeared, the skeleton surface area is

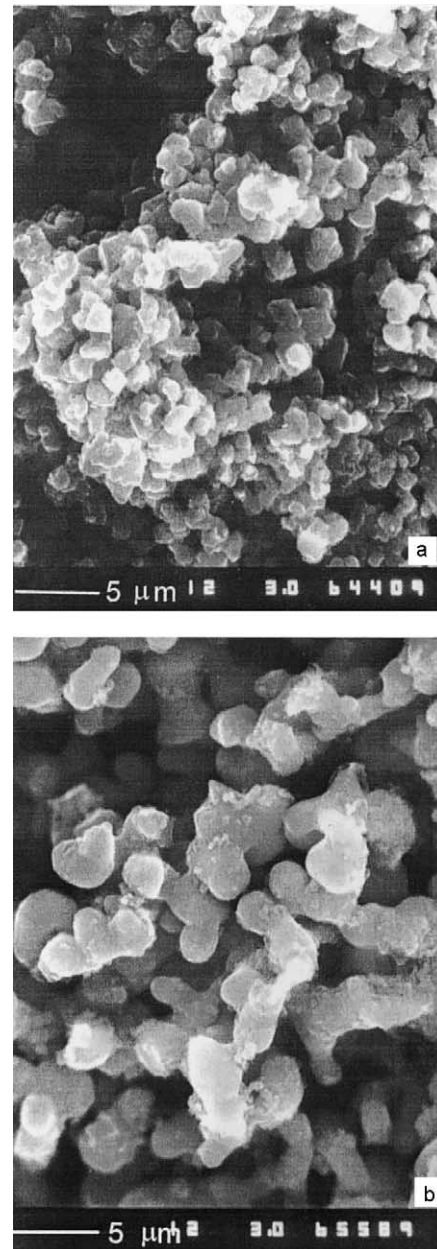


Fig. 13. SEM analysis of PbSnCa negative plate (1.70 wt.% phenolic-OH group content in the lignin): (a) charged NAM before cycling; (b) charged NAM after cycling.

small and a comparatively small part of the lead participates in the discharge, which is responsible for the low capacity and thus the short cycle life of the battery.

4. Discussion of results

Is the correlation between the NAM surface and the capacity of the battery a direct one? Let us compare the specific surface data for both types of batteries, presented in Fig. 11, with their initial capacity performance before cycling (Fig. 1), third discharge. These data for the batteries

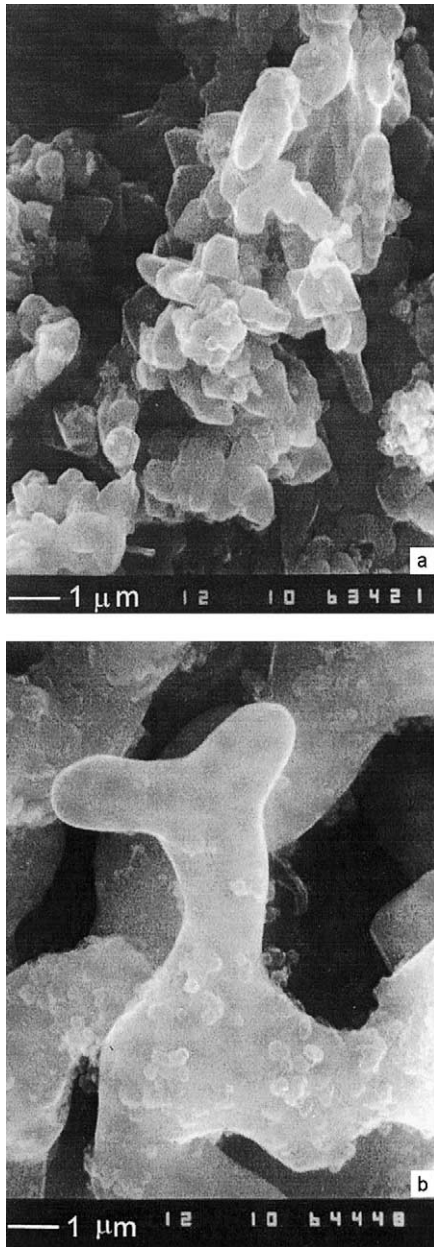


Fig. 14. SEM analysis of PbSb negative plate (0.28 wt.% phenolic-OH group content in the lignin): (a) charged NAM before cycling; (b) charged NAM after cycling.

with 1.20% phenolic content in the expander are given in Table 2.

The specific surface of NAM for the batteries with PbSb grids decreases by 4.0 m²/g, i.e. a 56% decrease as compared to the NAM surface before cycling, while the decrease in capacity is by 34%. In the case of batteries with PbSnCa grids, the NAM surface decrease is only by 0.13 m²/g (21% versus the initial NAM), while the capacity decrease is by 39.5%. These data indicate that the specific surface of NAM alone does not directly determine the capacity of the battery. There are other parameters, too, which influence the capacity performance.

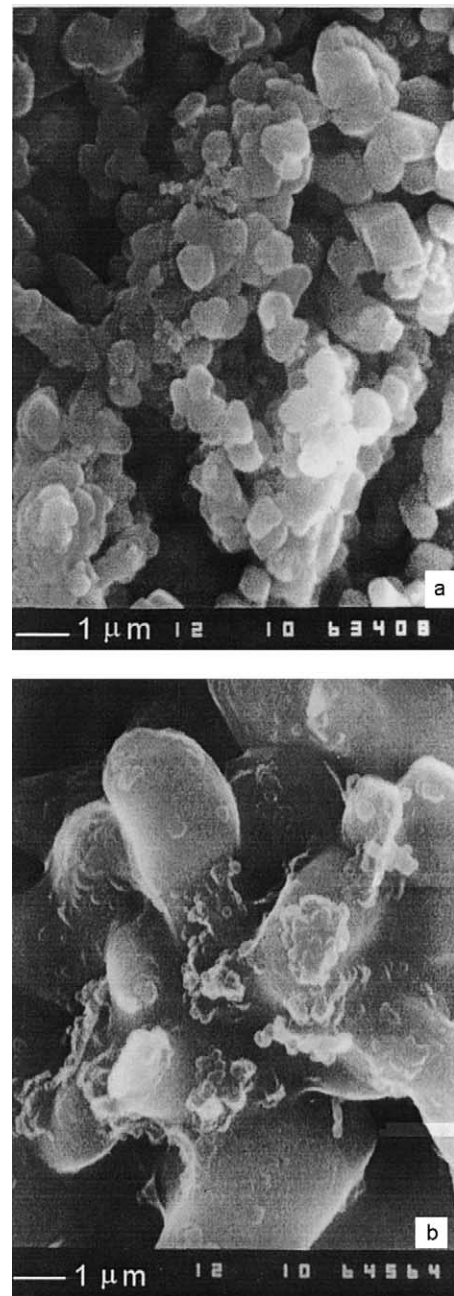


Fig. 15. SEM analysis of PbSb negative plate (1.70 wt.% phenolic-OH group content in the lignin): (a) charged NAM before cycling; (b) charged NAM after cycling.

Table 2
Specific surface area of NAM and battery capacity for the two types of batteries before and after cycling

	PbSb battery		PbSnCa battery	
	Surface (m ² /g)	Capacity (%)	Surface (m ² /g)	Capacity (%)
Before cycling	0.71	104	0.61	109.5
After cycling	0.31	70	0.48	70

The data in Table 2 show also that the changes in NAM surface area on cycling depend strongly on the type and amount of grid alloying additives used. The amount of expander changes on cycling as a result of degradation under the action of hydrogen, oxygen and the strongly negative potential [1]. Figs. 1-3, 5 and 7 provide evidence that the alloying additives interact with the expander. Hence, its nature changes and so does its involvement in the charge–discharge processes, thus influencing the capacity and cycle life performance of the battery.

5. Conclusions

During the initial tests, both the C_{20} capacity and the CCA performance depend on the content of phenolic groups in the expander as well as on the type and amount of additives in the grid alloy. These additives dissolve partially in H_2SO_4 and react with the functional groups of the expander forming metal–lignin compound(s). The latter exert an influence on the oxidation and deposition of Pb onto NAM during charge and discharge by impeding the formation of small Pb particles building up the energetic structure. This, in turn, affects the performance of the battery. Batteries with PbSb grids exhibit a decline in C_{20} capacity, CCA performance and cycle life, when the content of phenolic groups in the expander increases. The self-discharge and the charge acceptance of these batteries increase as well. In the case

of batteries with PbSnCa grids, some kind of metal–lignin compound is probably formed. Its activity with regard to capacity, cycle life and self-discharge of the batteries reaches a steady state at relatively small phenolic group content in the expander. Hence, the performance parameters of the negative plates are high and do not depend on the content of phenolic groups in the lignin. The results of the present investigation indicate that when selecting an appropriate expander for a particular battery application, the type and content of grid alloying additives should be taken into account.

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