

INFLUENCE OF ADDITIVES ON CATHODIC PROCESSES IN THE NEGATIVE ELECTRODE OF THE LEAD STORAGE CELL

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In this paper we report a study of the cathodic behavior of lead electrodes of the pasted type containing various organic surfactants, expanders, and inorganic additives, introduced into the paste before application.

The following expanders were studied: the tanning agent BNF [1], which is used in the USSR, the recently proposed DSV [2], humic acid, and induline. Tanning agent BNF is the product of condensation of crystalline phenol and β -naphtholsulfonic acid with formaldehyde. DSV is a desulfonated macromolecular fraction of resins from vanillin production. Humic acid was made from peat in Hungary. Induline, a dye derived from ammonium bases, was made in Italy. The inorganic additive used was BaSO_4 . Moreover, in view of the fact that Akuvit additive for electrolytes [3], containing a mixture of 10% $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$, 13% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 45% $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and 32% tartic acid, $\text{C}_4\text{H}_6\text{O}_6$, has been introduced and is in use in Hungary to improve battery charge and to diminish sulfating of plates, we investigated the influence both of this additive as a whole and of its individual components on the performance of the negative electrode.

Experimental cells each consisting of a single negative test electrode and two auxiliary positive electrodes $47 \times 47 \times 2.3$ mm were investigated. The cell assembly was of the open type (with excess electrolyte) to allow easy observation of the state of the electrodes, and to ensure that the electrode capacity was not limited by the amount of electrolyte. Two cells with the same composition of the active material in the negative electrodes were always tested simultaneously. The electrodes were made from S-0 grade lead, and the pastes from lead powder and chemically pure sulfuric acid. The additives were introduced into the paste in the following amounts (%) on the weight of dry lead powder: BaSO_4 0.4, BNF 0.4, DSV 0.35, humic acid 0.5, induline 0.35 and 1.0, Akuvit 1.7, $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ 0.17, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.225, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ 0.77, $\text{C}_4\text{H}_6\text{O}_6$ 0.54. After filling of the lead-antimony grid with paste the electrodes were formed in a solution of sulfuric acid (1.08 g/cm^3) at $7.5 \cdot 10^{-3} \text{ A/cm}^2$ current density.

Variations of the potentials of negative electrodes containing various organic additives during forming are shown in Fig. 1. The potentials were measured against a Cd reference electrode. Introduction of 1.0% of induline into the active material of the negative electrode shortens the time of change of the electrode potential from positive to negative values substantially (to 4.5 h), and such electrodes have the highest negative potential, -0.525 V , at the end of forming. However, this does not mean that electrodes containing induline are formed more rapidly than electrodes with other additives, because even at the end of forming the surface of negative electrodes is covered with a fairly considerable layer of PbSO_4 . Consequently, in presence of induline (1.0%) dissolution of PbSO_4 is hindered, evidently as the result of poisoning of the electrode by excess organic substance. Forming of electrodes with an induline content of 0.35% proceeds normally.

Forming of electrodes containing humic acid proceeds smoothly, the electrode surface is not coated with a layer of PbSO_4 , and the final potential has a lower negative value, -0.36 V , than in absence of additives. A constant potential becomes established on all the electrodes,

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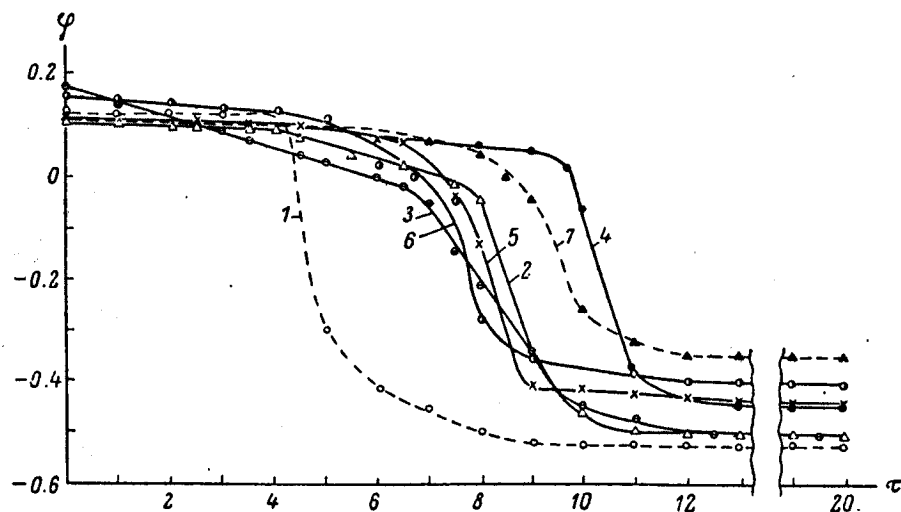


Fig. 1. Variations of the potential of negative electrodes during forming. φ) Potential (V); τ) time (h). 1) BaSO_4 + induline (1.0%); 2) BaSO_4 + BNF; 3) BaSO_4 + DSV; 4) without additives; 5) BaSO_4 ; 6) BaSO_4 + induline (0.35%); 7) BaSO_4 + humic acid.

with the exception of the electrode containing 1.0% of induline, after about 12 h, while an appreciable shift of potential in the negative direction (by 0.1-0.15 V), indicating considerable retardation of plate charging, occurs after 6-10 h (Fig. 1).

After the forming the electrolyte was replaced by electrolyte of 1.28 g/cm³ density (9.6 N H_2SO_4 solution) and the cell was fully charged at $9 \cdot 10^{-3}$ A/cm² current density.

The following preliminary treatment was used for investigation of the influence of various additives on charging of the cells. The cell was first subjected to prolonged discharge (about 3-4 h) at $11 \cdot 10^{-3}$ A/cm² current density until the potential of the negative electrode reached 0.5 V, and the duration of discharge (capacity) was recorded. The cell was then fully charged again, and discharged to 50% of the recorded capacity. The half-discharged cell was then kept idle for 2 h, after which it was charged at a constant voltage of 2.4 V cross the cell; variations of the current strength of the potential of the negative electrode were recorded during the first 10 min of the charging. This method of charge testing is laid down in the technical specifications of the Fiat firm [4] for assessment of the charge characteristics of batteries. It is considered that good charging of starter batteries for VAZ passenger automobiles is ensured if the charge current for a 12-V battery determined by this method 10 min after the start of charging at 14.4 V is not less than 6.9 A (with the assumption that the current density calculated for the apparent area of the negative electrodes is not less than $3.3 \cdot 10^{-3}$ A/cm²). We previously established experimentally that to satisfy this condition the charge current of the experimental cell at the 10th minute should be not less than 900 mA (or a current density of $2.0 \cdot 10^{-2}$ A/cm², as the cell was made with excess electrolyte and with an excess number of positive electrodes while the current density was calculated on the area of the negative electrode). The constant voltage of 2.4 V supplied to the cell was monitored with a voltmeter of the M106 type, class 0.5. The current strength was measured at 1-min intervals for 10 min with an ammeter type M104, class 0.5, and the potential of the negative electrode was measured with an R-307 potentiometer against a mercurous sulfate reference electrode. The sulfuric acid concentration in the reference electrode was the same as in the test cell (9.6 N). Plots of the logarithm of the current density against the charging time for electrodes with various additives are shown as examples in Fig. 2. Similar curves were obtained for other systems. Values of the charge current density at the 10th minute with all the additives tested are given in Table 1. It follows from Fig. 1 and Table 1 that the charge current at the 10th minute is highest for negative electrodes with additives or containing BaSO_4 . Of the additives investigated, only DSV and humic acid ensure a charge current density of the order of $2 \cdot 10^{-2}$ A/cm². Cells whose negative electrodes contain BNF or induline will be charged more slowly than with DSV and humic acid as additives. The potentials of the negative electrodes were also measured for 10 min during the charging. It was observed that during this time the electrode potential changes by only

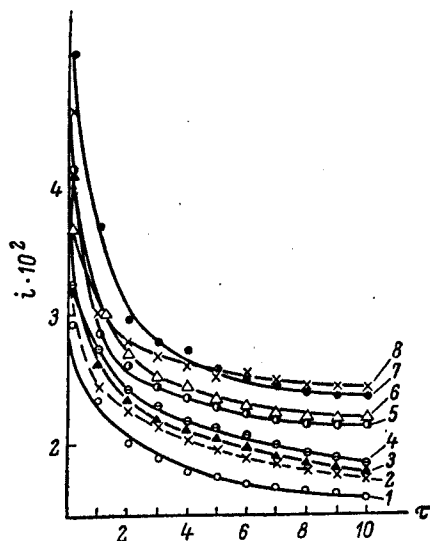


Fig. 2

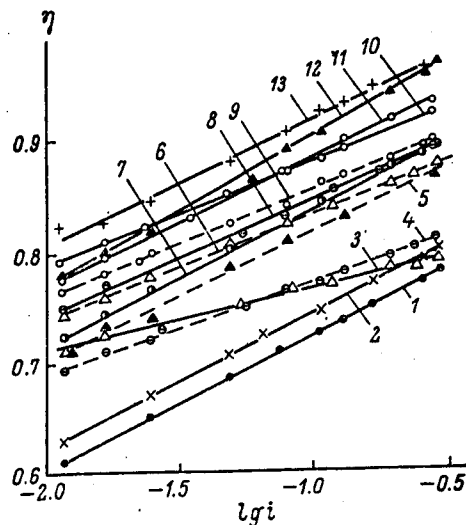


Fig. 3

Fig. 2. Variations of current density during 10 min of charging of experimental cells at a constant voltage of 2.4 V. 1) Current density (A/cm^2); τ) time (min). 1) $BaSO_4$ + BNF; 2) $BaSO_4$ + induline + $CdSO_4$ + $MgSO_4$ + $Al_2(SO_4)_3$; 3) $BaSO_4$ + induline + $Al_2(SO_4)_3$; 4) $BaSO_4$ + induline; 5) $BaSO_4$ + humic acid; 6) $BaSO_4$ + DSV; 7) without additives; 8) $BaSO_4$.

Fig. 3. Hydrogen overpotentials at negative electrodes. η) Hydrogen overpotential (V); 1) current density (A/cm^2). 1) Without additives; 2) $BaSO_4$; 3) $BaSO_4$ + Akuvit; 4) $BaSO_4$ + BNF + $Al_2(SO_4)_3$; 5) $BaSO_4$ + humic acid + $CdSO_4$; 6) $BaSO_4$ + BNF + Akuvit; 7) $BaSO_4$ + humic acid; 8) $BaSO_4$ + humic acid + $Al_2(SO_4)_3$; 9) $BaSO_4$ + BNF + $C_4H_6O_6$; 10) $BaSO_4$ + BNF; 11) $BaSO_4$ + humic acid + $MgSO_4$; 12) $BaSO_4$ + induline; 13) $BaSO_4$ + DSV.

10-30 mV from the equilibrium value.

It is seen from the data in Table 1 that Akuvit additive raises the charge current density at the 10th minute for electrodes containing BNF tanning agent from $1.5 \cdot 10^{-2}$ to $1.9 \cdot 10^{-2}$ A/cm^2 , but does not quite ensure the required value of $2 \cdot 10^{-2}$ A/cm^2 . It follows from the data in Table 1 that all the components of Akuvit raise the charge current density for electrodes with BNF; $Al_2(SO_4)_3$ has the strongest effect. Additions of Cd, Mg, and Al sulfates have virtually no influence on the charge current density for electrodes containing $BaSO_4$ and humic acid or induline in the active material.

No lead compounds except $PbSO_4$ were detected by x-ray structure analysis in any of the active materials studied.

For determination of the influence of the various additives on the practical capacity of the cells, the latter were subjected to alternating charge and discharge cycles. It was of interest to determine the capacity of the negative electrodes under starter operating conditions, as this capacity limits the capacity of the whole battery under such conditions and depends strongly on the additives introduced into the active material. The cells were discharged at $1.5 \cdot 10^{-1}$ A/cm^2 current density to a potential of 1.0 V of the negative electrode against a Cd reference electrode. The cell discharge time (capacity) under starter conditions at $t = 25^\circ$ in the fifth cycle is shown in Table 1. The highest capacities were found for cells whose negative electrodes contain DSV together with $BaSO_4$ (10.2 min), BNF with $BaSO_4$ (8.5 min), and BNF with $BaSO_4$ and the Al salt (9.1 min). Cells with electrodes containing $BaSO_4$ and induline have a capacity of 7.2 min, and with electrodes containing humic acid with $BaSO_4$ and with added salts, about 7 min, which is considerably less than with BNF and DSV. It is interesting to note that introduction of tartaric acid into the active material of an electrode containing BNF together with $BaSO_4$ lowers the cell capacity sharply. It is evidently owing to the presence of tartaric acid that Akuvit additive lowers cell

TABLE 1

Additive in active material of negative electrode	Charge curr. dens. $\cdot 10^2$ at 10th min (A/cm ²)	Disch. time in 5th cycle (min)	Hydrogen overpot. (V) at $\log i = -2$	Constant b of reaction of hydrogen evolution (V)
Without additives	2.3	1.6	0.61	0.12
BaSO ₄	2.3	2.24	0.63	0.12
BaSO ₄ + BNF	1.5	8.5	0.79	0.095
BaSO ₄ + DSV	2.0	10.25	0.81	0.115
BaSO ₄ + humic acid	2.0	6.5	0.72	0.125
BaSO ₄ + induline	1.7	7.2	0.78	0.135
Akuvit	1.9	0.9	0.68	0.085
BaSO ₄ + Akuvit	2.5	1.5	0.71	0.055
BNF + Akuvit	1.9	6.75	0.72	0.10
BaSO ₄ + BNF + Akuvit	1.9	7.45	0.74	0.095
BaSO ₄ + BNF + CdSO ₄	2.0	8.0	0.71	0.11
BaSO ₄ + BNF + MgSO ₄	1.9	8.1	0.71	0.115
BaSO ₄ + BNF + Al ₂ (SO ₄) ₃	2.2	9.05	0.69	0.085
BaSO ₄ + BNF + C ₄ H ₄ O ₆	1.7	6.9	0.76	0.095
BaSO ₄ + BNF + CdSO ₄ + MgSO ₄ + Al ₂ (SO ₄) ₃	2.0	9.05	0.71	0.10
BaSO ₄ + humic acid + CdSO ₄	2.0	7.4	0.71	0.12
BaSO ₄ + humic acid + MgSO ₄	2.0	7.75	0.77	0.115
BaSO ₄ + humic acid + Al ₂ (SO ₄) ₃	1.9	7.1	0.75	0.105
BaSO ₄ + humic acid + CdSO ₄ + MgSO ₄ + Al ₂ (SO ₄) ₃	2.0	6.85	0.73	0.13
BaSO ₄ + induline + Al ₂ (SO ₄) ₃	1.7	7.7	0.76	0.135
BaSO ₄ + induline + CdSO ₄ + MgSO ₄ + Al ₂ (SO ₄) ₃	1.7	7.7	0.73	0.14

capacity considerably, while additions of Cd or Mg sulfates produce only a slight decrease of capacity.

It follows from our results that only the expanders DSV and humic acid together with BaSO₄ ensure a charge current density of the order of $2 \cdot 10^{-2}$ A/cm². Additions of aluminum and cadmium salts to active electrode material with BNF raise the charge current density adequately.

However, electrodes with humic acid and with BNF together with BaSO₄ have lower capacity under starter conditions than electrodes with DSV.

It was of interest to find how the additives studied influence the hydrogen overpotential at the negative electrodes of the lead cell. The hydrogen overpotential was measured with the use of a bridge circuit, with the aid of an R-307 potentiometer and an M195/1 galvanometer. Data on the hydrogen overpotential (η) are plotted in Fig. 3, and values of the constant b of the Tafel equation and of η at $\log i = -2$ are given in Table 1.

It is seen from Fig. 3 and from the data in Table 1 that the highest values of η are obtained on negative electrodes containing BaSO₄ and the expanders DSV, induline, and BNF in the active material. Of these, BNF gives the smallest slope b of the overpotential curve, resulting in relatively smaller self-charge at a lower final charge voltage. Addition of Akuvit to the active material of an electrode containing no additives other than BaSO₄ greatly increases the hydrogen overpotential at low current densities (by 85 mV at $\log i = -2$) without changing it appreciably at high current densities. The constant b for electrodes without additives and with BaSO₄ only is 0.12 V, which is in agreement with literature data [5, 6], while for electrodes with added Akuvit and BaSO₄ it is 0.055 V. Thus, addition of Akuvit greatly diminishes the slope of the hydrogen-overpotential curves and therefore produces a greater relative increase of the hydrogen overpotential at low current densities, which should diminish self-discharge of the batteries. However, Akuvit cannot replace expanders, and it is seen from Fig. 3 that introduction of Akuvit into the active material of an electrode containing BaSO₄ together with BNF does not diminish the slope of the curve (0.095V), but merely lowers the hydrogen overpotential uniformly by 50 mV.

We also investigated the influence of addition of Cd, Mg, and Al sulfates and of tartaric acid (C₄H₄O₆) on the hydrogen overpotential η at electrodes containing BaSO₄ together with BNF. All these additives lower η , and the lowering is especially pronounced on addition of Al₂(SO₄)₃; for example, at $\log i = -2$ it amounts to 100 mV. Addition of Al₂(SO₄)₃ diminishes the slope of the curves slightly. However, this additive produces a large decrease of the hydrogen overpotential even at low current densities, and consequently increases self-discharge.

Figure 3 (curves 5, 7, 8, and 11) and Table 1 show the results of measurements of η at electrodes containing BaSO_4 in the active material together with humic acid and also with Cd, Mg, and Al sulfates. Introduction of MgSO_4 (curve 11) raises the hydrogen overpotential by about 50 mV. The cadmium salt (curve 5) lowers η slightly, while the aluminum salt and the salt mixture raise it a little. Introduction of a mixture of the Cd, Mg, and Al salts into the active material of the electrode containing BaSO_4 together with induline, as shown in Table 1, lowers the hydrogen overpotential by 50 mV. The curves for the hydrogen overpotential on electrodes containing BaSO_4 together with induline or BaSO_4 with induline and Cd, Mg, and Al sulfates have a greater slope (0.135-0.140 V) than the curves for electrodes with BNF and DSV; this should have an adverse effect on battery performance (increase of self-discharge and of the final charge voltage).

CONCLUSIONS

1. In studies of forming of negative electrodes with four different additives it was found that the best results are obtained with electrodes containing humic acid (from Hungary); their final forming potential is lower by 150 mV than for electrodes with BNF and DSV, and by 175 mV than for electrodes with induline (1.0%).

2. The expanders DSV and humic acid jointly with BaSO_4 ensure a charge current at the 10th minute (of the order of $2.0 \cdot 10^{-2} \text{ A/cm}^2$) equal to the so-called "minimum" charge current. The charge current of electrodes with the expanders BNF and induline is lower than the minimum permissible value. Additions of Cd, Mg, and Al sulfates to the active material of electrodes containing humic acid or induline as expanders have no appreciable influence on the charge current.

3. Of all the organic expanders studied, DSV, induline, and BNF give great increase of the hydrogen overpotential at medium current densities while humic acid gives the least; however, the latter gives the greatest self-discharge. Addition of Akuvit, as of $\text{Al}_2(\text{SO}_4)_3$, diminishes the slope of the hydrogen-overpotential curves for electrodes containing humic acid) in presence of BNF it leads to considerable lowering of the hydrogen overpotential even at low current densities and consequently increases self-discharge.

4. The greatest capacity of negative plates in presence of excess electrolyte is obtained with the use of the expander DSV and also of the expander BNF with added salts.

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