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Electrochemical characterisation of expander materials

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Abstract

A method is proposed for the characterisation of expander materials based on the comparison of the results of three different electrochemical techniques: electrochemical impedance, cyclic voltammetry and potentiostatic transients. The evaluation of the expanders performance carried out on the basis of the results of such techniques takes into account different important actions of the organic additives such as adsorption on lead and the kinetics of electrochemical reactions, which are all very important for the practical behaviour of the expanders in the negative plate of the lead–acid battery. The need of clarifying possible correlations between chemical characterisation and electrochemical tests is shortly discussed. This last point is mainly focused on the understanding of the action of the functional groups which are present in the organic molecules.

Keywords: Electrochemical techniques; Lead–acid batteries; Organic expanders; Negative plate

1. Introduction

Expander materials are added to the negative plate of lead–acid batteries with the aim of increasing the apparent volume of the active material, which results in an increased performance at high discharge rates and cyclability.

Though the expander materials are commonly a mixture of inorganic and organic substances, in this paper the discussion will be limited to the organic components, which act as dispersant agents by maintaining a highly porous active mass. They also exert other beneficial effects on the behaviour of the negative plate by influencing the hydrogen overpotential and inhibiting the effects of impurities.

In spite of the vast amount of works reported in the literature, the mechanism of action of the organic expanders is not yet completely understood, mainly because of the complexity of the system and the variability of the organic substances, derived from different natural products, whose composition is not clearly defined. It is commonly accepted that adsorption of such substances on the lead crystals [1–6] favours a dissolution–precipitation mechanism for lead sulphate formation, thus preventing passivation by a solid state reaction, [7–11]. Works by Ritchie [4,5] and Willihnganz [3] indicate that the effects of organic expanders can be explained by considering that a more porous lead sulphate is formed during discharge as a consequence of the partial coverage of the lead surface by adsorption of the organic substance, while finer lead crystals are formed during charge.

Literature works have not clarified the debate on the importance of the adsorption of organic expanders on lead sulphate, but in some cases, see for example the work by Sharpe [6], direct measurements showed that adsorption on lead sulphate is of minor importance.

Though there is no doubt that tests performed on negative plates or on batteries are the only possible way to obtain comparable data of the operating condition, the understanding of the basic mechanisms of action of the expanders must be investigated on more simple systems by performing laboratory tests with flat lead electrodes immersed in sulphuric acid containing known amounts of dissolved expanders.

According to this approach a possible scheme for the investigation of the expanders' action should include separate experimental tests to check the adsorption strength, the influence of the expander on the kinetics of lead-sulphate formation and reduction, and chemical characterisation of the functional groups.

Different electrochemical techniques can be specifically employed to investigate the organic expanders and to compare their effects. Among them, those based on cyclic voltammetry, on potentiostatic transients and on impedance spectroscopy proved to be particularly successful.

The principal difficulties which arise in this type of investigation are due to the limited solubility of the organic compound and the reproducibility of the system. For each expander the solubility markedly changes with temperature

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and the solution pH. The majority of the commercially available organic expanders (lignosulphonates) present a very low solubility in concentrated sulphuric acid solutions, so the concentration of the dissolved expanders cannot usually exceed 40 ppm. In addition, in these very strong acidic media, it is very difficult to know the nature of the dissolved species.

As far as the problem of data reproducibility is concerned, in order to obtain a quantitative comparison of different expanders, the analysis must be based on a large set of experimental tests, by applying a statistical treatment of the data.

In the present paper, previous findings [12,13] are discussed to show the feasibility of an investigation method for the selection of expander materials based on their chemical and electrochemical mechanism of action. It must be observed that before transferring the knowledge gained by such a method to practical formulations, a confirmation of its validity by electrical tests on batteries with negative plates containing the tested organic expanders is needed.

2. Experimental conditions

Electrochemical laboratory tests are carried out with high purity lead electrodes embedded in a resin in order to have a flat circular exposed area of about 1 cm^2. At the beginning of each test the working electrode, mechanically polished by emery paper, is subjected to cathodic polarisation at a constant potential of -1.20 V (versus Hg/Hg_2SO_4 electrode), until a steady current in the range of 0.1 mA is reached, in order to assure a clean lead surface, free of lead sulphate and oxide.

The addition of the expander under test is made by dissolving the organic substance in the acid solution to be used in the electrochemical cell. In order to favour the dissolution process, the lignosulphonate-type additives can first be dissolved in a small amount of 0.1 M NaOH, and then added to the electrolyte, whose sulphuric acid content must be properly adjusted.

For the impedance tests the electrode is preliminary polarised at -1.3 V (versus Hg/Hg_2SO_4 electrode) until a steady-state current is reached (about 20 min), then the impedance spectrum is measured in the frequency range 10^4–10^{-2} Hz with an amplitude of the sine signal of 5 mV. As soon as the first measurement carried out with pure sulphuric acid is done, a second run is performed after the addition of the chosen expander to the solution. The Solartron 1150 FRA connected to an AMEL mod. 5011 Potentiostat have been employed.

For cyclic voltammetry tests the voltage range -1.2 to -0.7 V (versus Hg/Hg_2SO_4 electrode) was chosen, so that the reactions at the lead electrode are completely developed within these limits, without significant release of hydrogen. The usual value of the potential scan-rate is 2 mV/s. Cycling is continued until a constant shape of the voltammogram is obtained, this condition is typically achieved after 400–800 cycles. By plotting the amount of charge corresponding to the area of the anodic peak versus the number of cycles, it can be observed that such charge steadily increases at the beginning. Then, at about 400 cycles, an almost constant value is reached. The plot of these final values of the amount of charge versus the expander concentration shows an increase up to a rather well defined plateau, where no further significant increase is observed. For the majority of the tested expanders, the concentration of the organic substance, marking the beginning of the plateau region, is about 20 ppm.

The experimental tests to study the formation of lead-sulphate by means of potentiostatic transients require a multi-step procedure. First, the lead electrode is polarised at a potential of -1.2 V (versus Hg/Hg_2SO_4 electrode) for 30 min to obtain a complete reduction of its surface, then the potential is stepped to -0.89 V (versus Hg/Hg_2SO_4 electrode). The duration of this final step, during which the recording of the current intensity takes place, can typically vary from 10 to 100 s. For improving the reproducibility of the results, this procedure is repeated three times with the blank solution, then 20 ppm of the expander are added to the electrolyte and three other similar oxidation/reduction cycles are carried out.

3. Discussion of the electrochemical techniques

The use of different electrochemical techniques aims at obtaining an overall characterisation of the expander materials accounting for the different actions which they exert on the lead electrode. The comparison of data provided by those techniques, namely impedance measurements, cyclic voltammetry and potentiostatic transients can be the basis for defining a reliable method for the selection of the expander materials. This is supported by the observation that results of impedance measurements, carried out at cathodically polarised lead electrodes, provide important information about the adsorption of the organic additives on lead, cyclic voltammetry, in addition to other important electrochemical aspects, is suitable for characterising the formation of sponge lead on the initial flat surface in the presence and in the absence of the additives, while the transient behaviour for lead-sulphate formation gives specific information on the influence of the additive on the reaction kinetics.

A short description of the electrochemical techniques, focused on the characterisation of organic expanders, is given in the following. For a more complete understanding of such topic, see [12,13] and references therein.

3.1. Impedance measurements

To investigate the adsorption of organic substances on lead, stationary polarisation curves or electrochemical impedance can be usefully employed. The measurements must be carried out at sufficiently negative potentials where, due to slight hydrogen evolution, no lead-sulphate is present on the electrode surface. Both methods provide similar information because the value of transfer resistance of the hydrogen evolution reaction equals the ratio of the slope of the $V/\log I$ curve (Tafel slope) and the stationary value of the current intensity for which the determination of the transfer resistance R_t has been carried out:

$$\frac{dV}{d\log I} = b = R_t I.$$

The frequency range for impedance measurements must be sufficiently wide in order to obtain the accurate values of the transfer resistance and double layer capacitance from the impedance spectra. In order to compare the effectiveness of the expanders, the ratio I/I_{exp} between the steady-state value of the cathodic current intensity without expander and in the presence of the expander, and the similar ratio R_{exp}/R between the transfer resistance value measured in the presence and absence of expanders have been computed. The influence of the expanders on the double layer capacitance is also a valuable information of the adsorption process.

3.2. Cyclic voltammetry

Von Borstel et al. [14] have discussed the great interest of applying cycling voltammetry to the characterisation of organic expanders. According to their indications, a lead electrode immersed in the sulphuric acid solution containing the expander is cycled within the potential range −1.3 to −0.7 V (SSE) with a sweep rate between 2 and 20 mV/s. During the voltammetry the anodic amount of charge is recorded and the data are analysed to obtain, according to the authors' definition, information on the "efficiency" and "stability" of the expander under test.

The computation carried out by Mac Donald [15] shows that, in the case of an electrode on which a resistive layer is formed, the trend of a voltammetric curve $i(V)$, traced by a linear potential scan, depends on the change of the layer resistance. According to such interpretation, the slope of the voltammetric curves is affected by the porosity and thickness of the layer which is being formed. In the case of lead in sulphuric acid the changes of the contact resistance are caused by the lead sulphate layer.

According to this model, the voltammetric curves are characterised by a pronounced asymmetry, since a drastic fall of the current intensity occurs when the coverage of the electrode surface by the resistive layer approaches unity. By considering the values I_p and E_p of the anodic peak current and corresponding potential it should be possible, in principle, to obtain, as indicated by Hampson and Lakeman [16,17], the porosity and thickness of the sulphate layer in the presence and in the absence of the expanders.

When considering the trend and shape of the voltammetric curves, it must be noted that the expanders modify both the anodic and the cathodic branches of the voltammetric cycle because in the former case they affect the structure of the formed lead-sulphate while, in the latter case, they exert an influence on the formation of lead crystals and on hydrogen evolution. In fact, during a voltammetric cycle carried out within a potential range in which the lead oxide is not formed, it can be observed that in the anodic branch of the cycle one single electrochemical reaction occurs. However, in the cathodic branch, hydrogen ion discharge partly occurs together with lead sulphate reduction. All three processes are influenced by the presence of expanders.

On the basis of the above considerations, it can be noted that, the voltammetric curves provide reliable information about the amount of charge stored in the anodic part of the cycle, i.e. on the formation of sponge lead, while they do not give direct kinetic information about single processes. As shown by Von Borstel [14], by plotting the amount of charge of the anodic peak as a function of the cycle number, a curve presenting a wide maximum is obtained. The difference between the maximum value of the amount of charge obtained in the presence of the expander and that obtained without the expander, has been related by the previous authors to the activity of the organic substance, while the difference between the number of cycles for which such maximum values are observed has been correlated to the stability of the expander.

3.3. Potentiostatic transients

This experimental technique consists in applying a potential step in the anodic direction to a lead electrode immersed in a sulphuric acid solution, starting from a completely reduced lead surface, and recording the change of the current intensity with time. The process of lead-sulphate reduction can be similarly investigated by applying the potential step in the cathodic direction, starting from a potential at which a stable $PbSO_4$ layer has been formed. The interpretation of such transients can be carried out by the well known laws of electrocrystallisation [18] or by a more complex theory proposed by Varela et al. [19,20]. The comparison of the transients obtained in the presence and absence of the expander provides valuable information about the influence of the organic additive on the kinetics of lead-sulphate formation and reduction.

A typical current/time curve for a potentiostatic oxidation of lead to lead-sulphate presents a well defined asymmetric peak, at the beginning the current increases up to a maximum value, then it decreases continuously at a lower rate. It has been shown [12,13] that from the transient curves it is possible to determine the value of $K\sqrt{N}$, where K is the rate constant of the oxidation reaction and N is the number of nucleation centres. This factor is inversely proportional to the time $t_{\max}$ required to reach the anodic peak current caused by the oxidation potentiostatic step. The ratio between the values of $t_{\max}$ measured in the absence and in the presence of expanders provides substantial information about their influence on the kinetics of the anodic process. The higher is $t_{\max}$ the more the electrocrystallisation is hampered, due to a lower value of the factor $K\sqrt{N}$. Thus, such ratio can be assumed for evaluating the efficiency of the expanders.

4. Results and discussion

To illustrate the potentiality of the proposed method for expanders' characterisation, some experimental results obtained by the above described techniques will be presented here. Most of them are taken from previous work [12] and have already been discussed.

Figs. 1 and 2 show the Nyquist plots of impedance data for a lead electrode in absence and in presence of two expanders, which both proved to be rather effective, but present different responses. The expander tested in Fig. 1 has the commercial name of DD5 and corresponds to a Kraft lignosulphonate, while in the test of Fig. 2 the commercial material UP298 has been used, which is a modified Vanisperse A. As previously mentioned, to obtain a quantification of the effectiveness of the expanders from impedance data, the ratio R_{exp}/R between the transfer resistance value measured in the absence and presence of expanders have been computed. The data reported in Figs. 1 and 2 indicate that for DD5 a value of 3.83 was found, while in the case of UP298 a value of 1.87 was obtained.

Fig. 3 shows the voltammograms of lead in 1.25 g cm^{-3} density sulphuric acid without additives, while Fig. 4 presents the cyclic voltammograms measured when 20 ppm of Vanisperse A were added to the electrolyte. These results allow to point out interesting features of the cyclic voltammetry behaviour when the expander is present with respect to the pure electrolyte situation. Without expander, the anodic peak-current increases to a limited extent on cycling, up to about 300 cycles and then it remains almost constant;

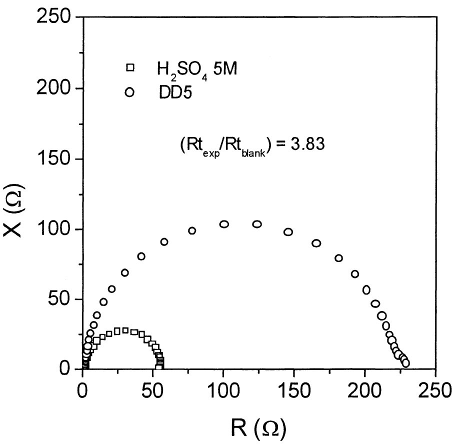

Fig. 1. Impedance data on the Nyquist plot determined in the frequency range 10^4–10^{-2} Hz, in 5 M sulphuric acid with and without the addition of expander DD5.

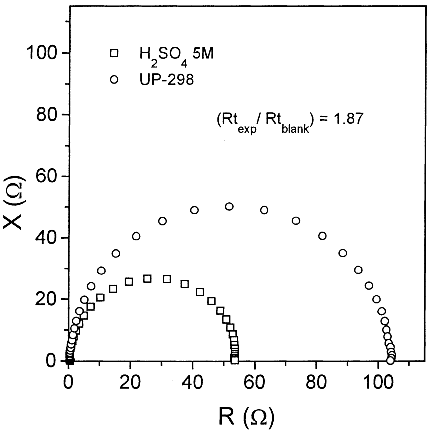

Fig. 2. Impedance data on the Nyquist plot determined in the frequency range 10^4–10^{-2} Hz, in 5 M sulphuric acid with and without the addition of expander UP-298.

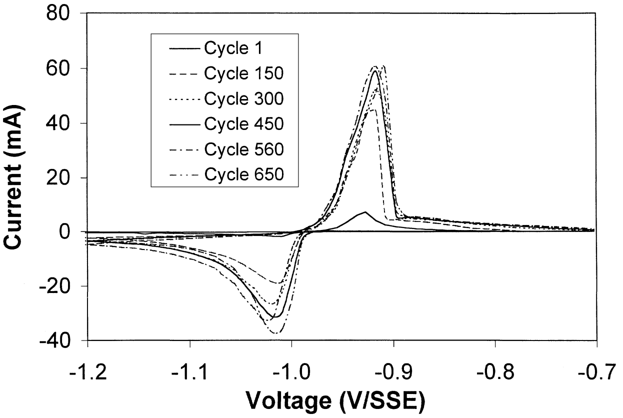

Fig. 3. Cyclic voltammograms of a pure lead electrode in 1.25 g cm^{-3} density sulphuric acid.

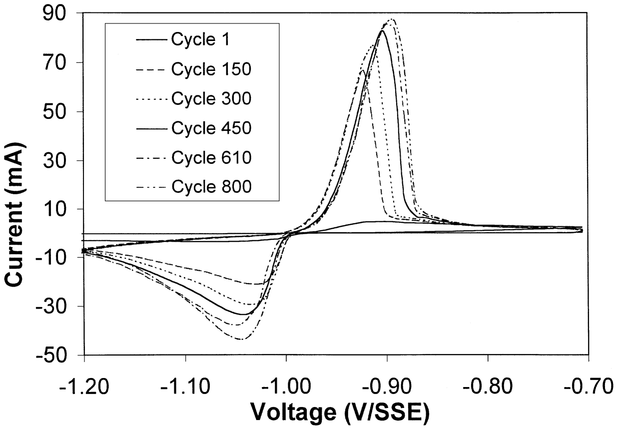

Fig. 4. Cyclic voltammograms of a pure lead electrode in 1.25 g cm^{-3} density sulphuric acid containing 20 ppm of Vanisperse A.

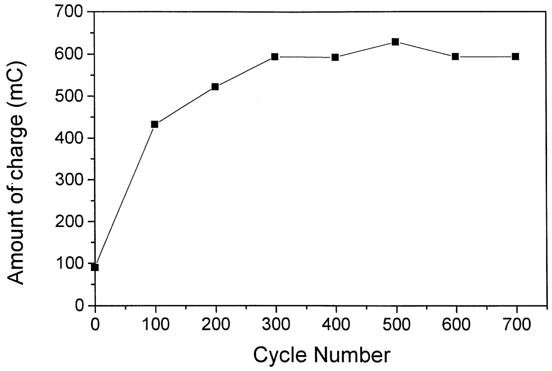

Fig. 5. Amount of charge of the anodic peak vs. number of cycles for a pure lead electrode in 1.25 g cm^{-3} density sulphuric acid.

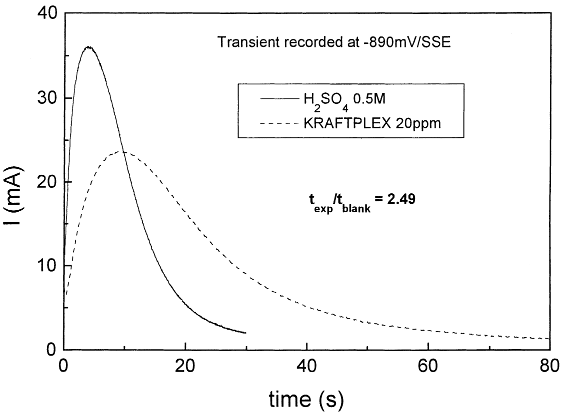

Fig. 7. Oxidation potentiostatic transient recorded at −0.89 V/SSE in 0.5 M sulphuric acid with and without expander Kraftplex.

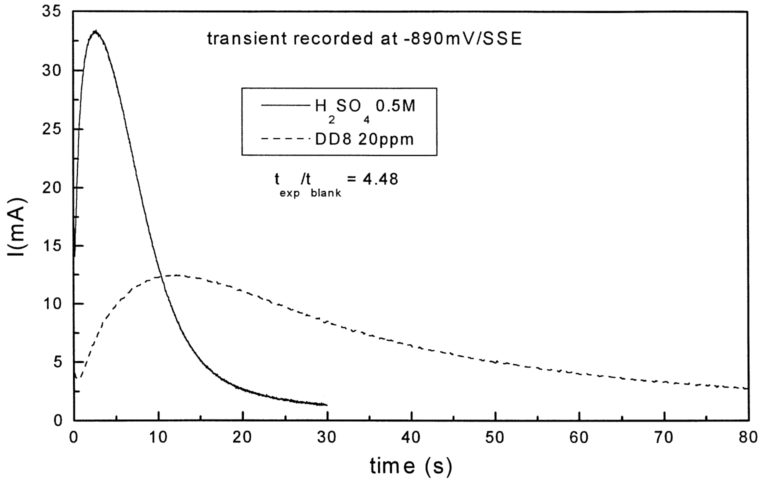

Fig. 6. Oxidation potentiostatic transient recorded at −0.89 V/SSE in 0.5 M sulphuric acid with and without expander DD8.

apart from the very beginning, the position of the peak is not changed. On the contrary, when the expander is present, the anodic peak-current continues to increase up to about 600–700 cycles and reaches much higher values. In addition a remarkable broadening of the anodic peak is observed with a shift of the peak-potential towards positive values. Some modifications are also visible on the cathodic branch: in the presence of the expander the cathodic peak is broader, and presents some shift on cycling towards negative potentials.

The change of amount of charge corresponding to the anodic peak area with the number of cycles is illustrated in Fig. 5. It can be seen that such charge steadily increases at the beginning, then, at about 400 cycles, an almost constant value is reached. Thus, the value of the anodic peak area at 600 cycles has been used for comparing the behaviour of the different expanders.

Examples of potentiostatic oxidation transients measured for two different expanders are shown in Figs. 6 and 7. On each diagram both plots, in the presence and in the absence of the expanders are reported. As previously described, from the ratio t_{exp}/t_{blank} of the time required to reach the current peak, measured with and without the organic additive, it is possible to quantify the expander's efficiency. Fig. 6 refer to expander DD8 which gave a value of 4.48 for the above ratio. Fig. 7 illustrates the results obtained with the expander Kraftplex, which is a typical sodium lignosulphonate obtained from waste pulp liquors. For this last expander a value of 2.49 was observed for the ratio t_{exp}/t_{blank}.

5. Conclusion

Since each experimental technique, as above described, provides some specific information on a particular action of the expanders, which is thought to be of importance for the overall efficiency, the whole picture deriving from the different experiments must be analysed.

The proposed scheme can be applied to obtain reliable information when comparing a number of different organic expanders in order to select the best candidates for practical testing in batteries. According to this view, after performing a complete set of experiments on each expander, a grid ranking the effectiveness of all expanders for each specific test must be constructed. The selection can be done by considering the expanders which are found in the top positions for every type of test. With reference to previously published data with seventeen different organic materials [12], we can affirm that the proposed approach proved to be of practical interest.

One point of major importance, which is not discussed in this paper, is the possibility of finding some correlation between the results of chemical and electrochemical characterisation. Some work is in progress on this subject and we have preliminary observed that the relative importance of the hydrophobicity and the polarity of the expanders is a key factor for explaining their efficiency in the negative plate. The non polar fraction of the organic molecule, mainly constituted by aromatic rings, can be easily adsorbed at the lead surface, leaving the polar groups, i.e. sulphonate and carboxyl groups, facing out to the aqueous electrolyte phase. Thus, the non polar part is important for covering metallic lead and lower the surface energy, so that formation of coarse crystals is energetically less favourable when compared to the situation in the absence of expanders. Polar groups can "trap" Pb^{2+} avoiding the formation of $PbSO_4$ crystals. This effect is mainly expressed by the sulphonate groups. These effects turn into an anti-flocculant action by preventing the recrystallisation of sponge lead, which leads to a coarsely crystalline structure of the negative plates.

The chemical characteristics of the expanders should be also considered for explaining the phenomena occurring during cycling. As the expanders are dispersed in an acid solution, ester hydrolysis reactions can occur and modify the organic molecules during the process. Hydrolysis can break the bonding of lignosulphonic acids with phenols and formaldehyde and create new hydrophilic groups, hence enhancing the performance of the expander during cycling operation of the battery.

As a final remark, it can be observed that though the real behaviour of expanders materials in the negative plate is much more complex than that observed with laboratory tests, a basic understanding of the chemical and electrochemical actions of the organic materials is of outmost importance for improving the formulation of expander materials in order to meet the performances required by novel applications.

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