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Density and hardness of negative pastes of lead–acid batteries containing organic additives with or without quinone structure

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Abstract

Density and hardness of the negative pastes of lead–acid batteries, to which organic compounds with or without quinone structures have been added, are investigated by means of the stick insertion depth test. Results show that the density and hardness of a paste containing anthraquinone are almost the same as one containing anthracene. By contrast, the two parameters are very different for pastes containing 1,2-naphthoquinone-4-sulfonic acid sodium salt and 1-naphthalenesulfonic acid sodium salt. Commercial lignin derivatives (Vanillex N, Vanisperse A, Indulin AT), which are used as additives for negative plates in lead–acid batteries, are also investigated by means of ultraviolet (UV) spectroscopy. It is found that these lignin derivatives contain quinone structures.

Keywords: Lead–acid battery; Organic expander; Quinone structure; Density and hardness of the negative paste; Stick insertion depth test; Ultraviolet spectra

1. Introduction

Lignin derivatives are typical additives for the negative active-material of lead–acid batteries. They affect the fluidity and plasticity of the negative paste, the ratio of different types of lead sulfate crystals (tribasic, tetrabasic) that are formed during mixing and curing, the performance of the lead–acid batteries, and so on. In recent years, lead–acid batteries have been operated in a partial-state-of-charge (PSoC) mode in several novel applications, such as hybrid electric vehicles [1,2]. Therefore, a more detailed understanding of the effect of additives is essential for obtaining the best performance from lead–acid batteries. In previous work, it was found that quinone structures in lignin derivatives, as well as in pure organic compounds, play an important role in the formation of a 'colloidal deposit' on a lead plate that had a surface oxide layer, and served as a model of leady oxide [3]. It was not clear, however, whether quinone structures actually affect the properties of the negative paste or not. Moreover, it was equally unknown whether lignin derivatives that are used in commercial lead–acid batteries have quinone structures, or not. In this study, the density and hardness of the negative paste of lead–acid batteries, to which some of organic compounds with or without quinone structures, have been added are investigated by means of the stick insertion depth test. The commercial lignin derivatives have been also examined by means of ultraviolet (UV) spectroscopy.

2. Experimental

2.1. Stick insertion depth test

For the stick insertion depth test, pure organic compounds rather than lignin derivatives were used in order to investigate the effect of functional groups in more detail. The organic additives were anthracene (Fig. 1(a)), anthraquinone (Fig. 1(b)), 1-naphthalenesulfonic acid sodium salt (NS, Fig. 1(c)), and 1,2-naphthoquinone-4-sulfonic acid sodium salt (NQS, Fig. 1(d)). The procedure of the test was as follows. At first, 600 g of leady oxide, 20 mmol of the pure organic compound (i.e., anthracene, anthraquinone, NS, or NQS) and 60 ml of water were mixed into a paste for 5 min. The stick insertion depth test was performed three times on each paste (result 1). Next, 12 ml of sulfuric acid solution (1.40 net. dens.) were added to each paste with mix-

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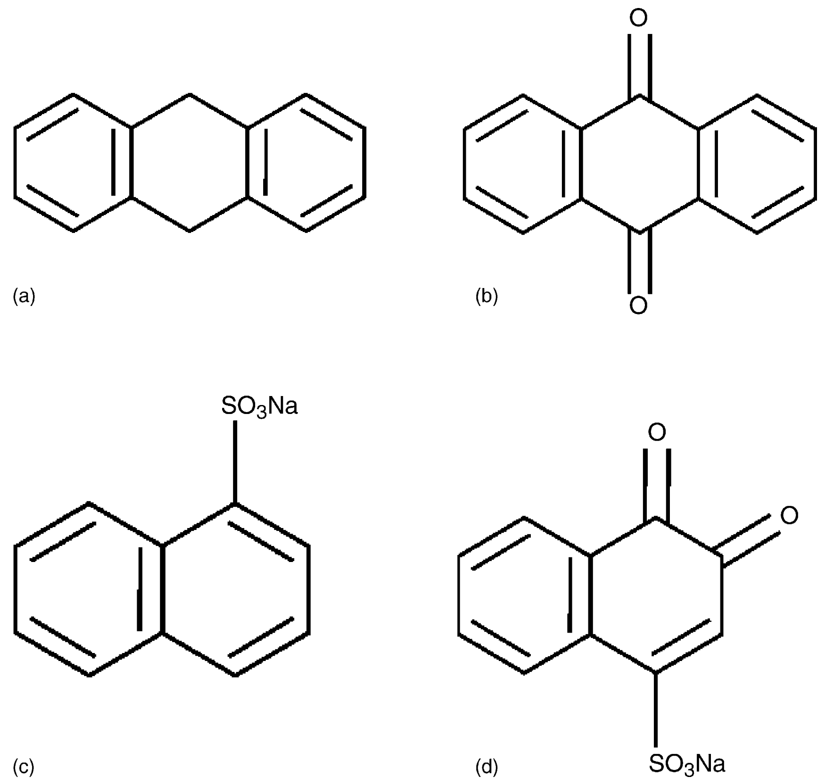

Fig. 1. Structures of organic additives used for stick insertion depth test: (a) anthracene; (b) anthraquinone; (c) 1-naphthalenesulfonic acid sodium salt (NS); (d) 1,2-naphthoquinone-4-sulfonic acid sodium salt (NQS).

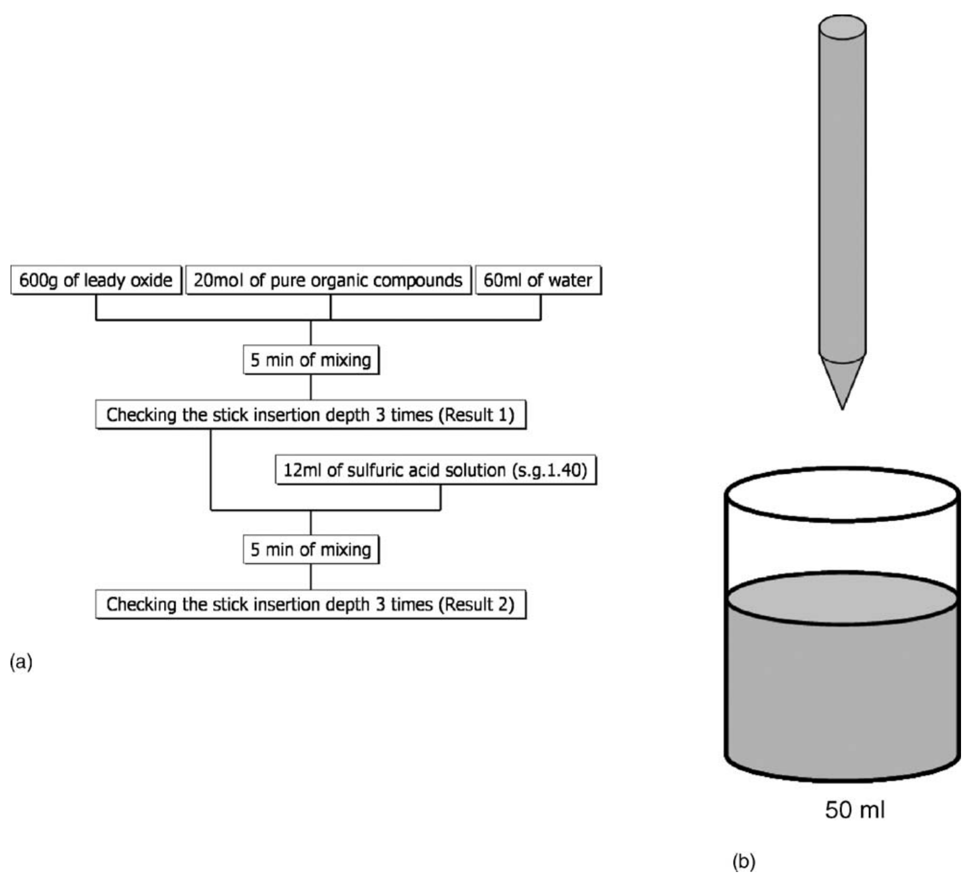

Fig. 2. Schematic illustration of (a) procedure and (b) equipment used for stick insertion depth test.

Table 1
Data obtained from stick insertion depth test

Additive	Result 1				Result 2			
	Paste density (g cm^{-3})	Stick insertion depth (mm)			Paste density (g cm^{-3})	Stick insertion depth (mm)		
		1st	2nd	3rd		1st	2nd	3rd
No additive	5.16	28	26	27	4.81	60	60	57
Anthracene	5.25	25	30	27	4.89	64	64	57
Anthraquinone	5.26	27	26	26	4.89	52	52	54
NS	5.20	57	57	48	4.75	74	77	81
NQS	5.04	>350	>350	>350	4.93	32	26	14

NS: 1-naphthalenesulfonic acid sodium salt; NQS: 1,2-naphthoquinone-4-sulfonic acid sodium salt.

ing for 5 min. Then, the stick insertion depth test was again conducted three times on each paste (result 2). A schematic illustrations of the test procedure and equipment are given in Fig. 2(a) and (b), respectively.

2.2. *Ultraviolet spectroscopy measurements*

Ultraviolet (UV) spectroscopy was performed on aqueous solutions containing lignin derivatives. Two types of the aqueous solution were used. The first was an alkaline solution (pH 12.2) that consisted of 0.2 ml of a solution of 0.053 g of a lignin derivative + 100 ml of 100 mM NaOH and 2.8 ml of a 100 mM NaOH. The second was an acid solution (pH 2.2) with 0.2 ml of 0.053 g of a lignin derivative + 100 ml of 50 mM H_3PO_4 and 2.8 ml of 50 mM H_3PO_4. The lignin derivatives used were Vanillex N (Nippon Paper Chemicals Co., Ltd.), Vanisperse A (Borregaard Ligno Tech), and Indulin AT (West Vaco).

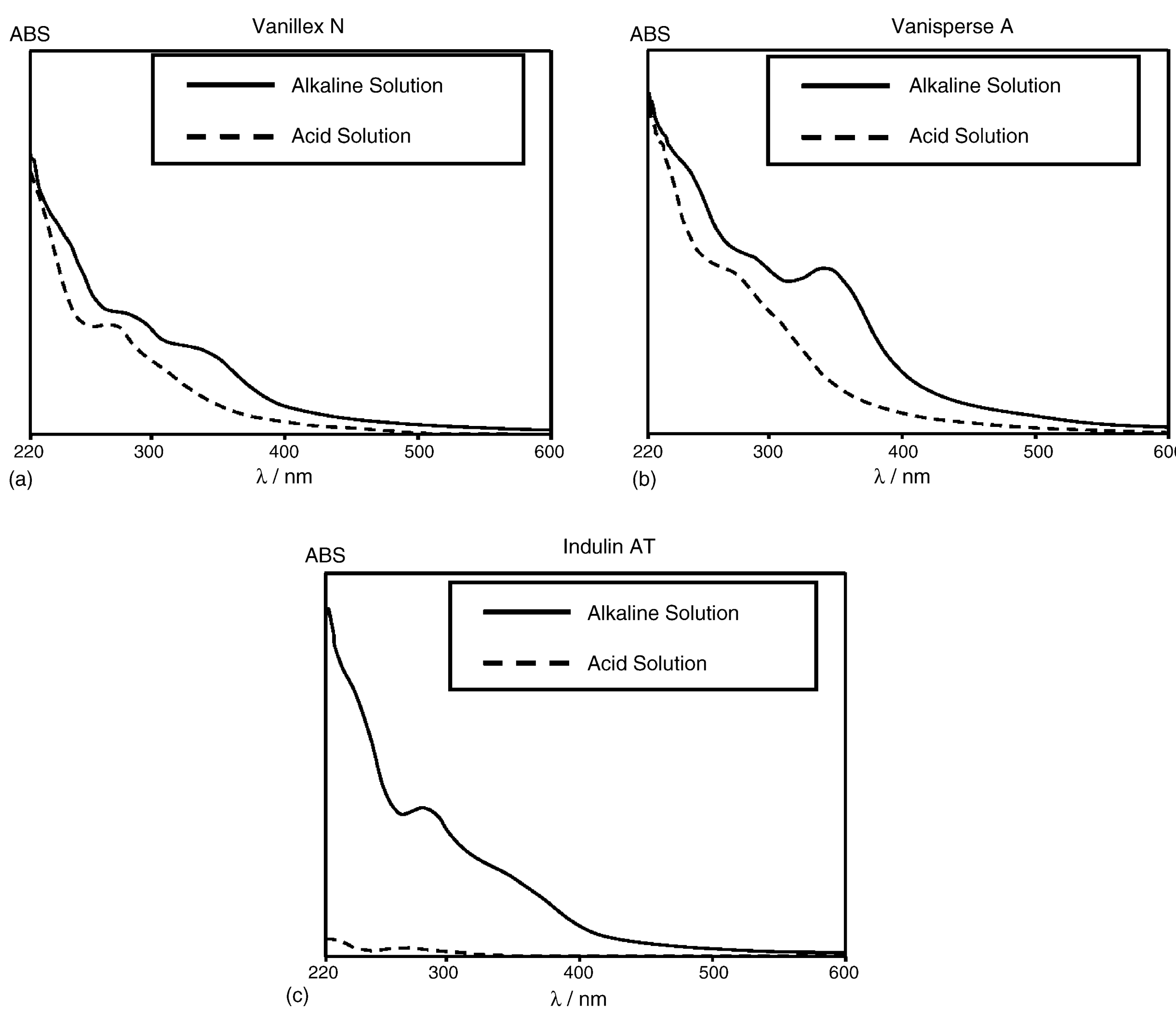

Fig. 3. UV spectra of aqueous solutions containing lignin derivatives: (a) Vanillex N; (b) Vanisperse A; (c) Indulin AT.

3. Results and discussion

3.1. Stick insertion depth test

The results of the stick insertion depth test are shown in Table 1. The more deeply the stick penetrates into the paste, the softer is the paste. It is found that the density and hardness of the paste containing either anthracene or anthraquinone are almost the same as those without additives, both before and after the addition of sulfuric acid solution (results 1 and 2). Before the addition of sulfuric acid solution (result 1), the paste containing 1-naphthalenesulfonic acid sodium salt (NS) is both denser and harder than that containing 1,2-naphthoquinone-4-sulfonic acid sodium salt (NQS). On the other hand, after the addition of sulfuric acid solution (result 2), the paste containing NS was less dense and softer than that containing NQS. Thus, it is not only the existence of quinone structures in organic additives but also the total structure of the organic additives that affect the density and hardness of the paste.

3.2. UV spectra measurement

The UV spectra of the aqueous solutions containing Vanillex N, Vanisperse A and Indulin AT are presented in Fig. 3(a)–(c), respectively. The UV spectra of all three alkaline solutions have an absorption maximum at 340 nm, as well as others at less than 300 nm. The absorption maximum at 340 nm is known to be caused by a quinone structure in the lignin derivative [4], so that it is concluded that Vanillex N, Vanisperse A and Indulin AT all contain a quinone structure.

4. Conclusions

The density and hardness of the negative pastes of lead–acid batteries, that contain organic compounds with or without quinone structures have been investigated by means of the stick insertion depth test. It is found that not only the existence of quinone structures in the organic additives but also the total structure of organic additives affects the density and hardness of the paste. Commercial lignin derivatives (Vanillex N, Vanisperse A, and Indulin AT) have also been characterized by means of UV spectroscopy. The results reveal that these lignin derivatives contain quinone structures.

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