

# The influence of construction of ionic liquid precursors containing bisulfate or sulfate anion on the rate of reaction creating electroactive paste used in lead acid battery

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## Introduction

Although lead-acid battery was invented over 150 years ago, it is still one of the most important chemical power sources [1]. The main substrate for electrode material in each lead-acid battery is lead powder, which is a mixture of lead oxide PbO and metallic lead Pb. In order to obtain an electroactive material, appropriate amounts of sulfuric acid, water, and additives are added to lead powder. The choice of additional ingredients (e.g. expanders, polypropylene fibres) depends on whether the prepared material is to be positive or negative. Moreover, the intended use of the battery sometimes requires the addition of different additives to pastes. Examples are start-stop system batteries that require the increase in the active material durability to allow start more often. Such an electroactive material is pasted in a grid, seasoned and electroformed. Obtaining an electrode material of high capacitance is, therefore, closely linked to the physicochemical properties of the lead powder used [1, 2].

The lead powder can be produced in ball mills (by mutual abrasion of metallic lead cylinders) or by means of a spraying method, where liquid lead is firstly “torn apart” with a propeller and then “taken” by a strong air stream, where it solidifies to the form of a powder (the so-called Barton reactors). During the production of lead powder, Pb is also oxidized to PbO to a level of approx. 70-80%. PbO has 2 variations  $\alpha$ - (red, tetragonal system) and  $\beta$ -PbO (yellow, rhombic system). The characteristic of lead powders depends on the method of their production. For example, powders produced in the Barton reactor have lower specific surface area and slightly different granulometric distribution. Maximum percentage of molecules shall be in the grain size range of 1-16  $\mu\text{m}$  [1].

Processes of paste generation by means of Barton pot method and curing give slightly different rate than by using ball mills.

The reactivity of lead powder with water and sulfuric acid is fundamental for the assessment of quality of this substrate in its application in the active material. One of the methods of testing the reaction of lead powder with sulfuric acid is the so-called reactivity at pH 4 [1, 3, 4].

The aim of the paper was to assess the effect of the addition of bisulfate and sulfate ammonium ionic liquid precursors to sulfuric acid on the rate of the formation of poorly soluble PbSO<sub>4</sub>, which results in the decrease in acidity and increase in pH from approx. 0.5 to 4. There was also an attempt to correlate the results obtained with the

values of electrolytic conductivity of ionic liquid precursors, which indicates the degree of dissociation of the compound in water and ion mobility.

Ionic liquids (ILs) and their precursors due to almost limitless possibilities of forming their physicochemical and biological properties are one of the most perspective development directions of the so-called “green chemistry”, therefore they are now widely used in many fields of the industry [5 ÷ 7]. The ILs are becoming more and more used in various types of chemical power sources, e.g. supercapacitors, ion-lithium cells, etc. [8, 9]. There are also literature reports regarding the studies on their application in lead-acid batteries [10, 11].

## Methods

The ILs tested included homologous series of protic ionic liquid precursors containing bisulfate and sulfate groups (Tab. 1). They were composed of carbon chains of the length of 6, 12 (or 14) and 16 atoms.

Table 1

Ionic liquid precursors used in research

Formula	Name	Designation
6 carbon atoms (C6)		
$\text{H}_{13}\text{C}_6-\text{N}^+\text{H}_2-\text{HSO}_4^-$	Hexyldimethylammonium bisulfate	HC6HSO4
$\text{H}_{13}\text{C}_6-\text{N}^+\text{H}_2-\text{SO}_4^-$	Di(hexyldimethylammonium) sulfate	HC6SO4
12/14 carbon atoms (C12/C14)		
$\text{H}_{29}\text{C}_{14}-\text{N}^+\text{H}_2-\text{HSO}_4^-$	Tetradecyldimethylammonium bisulfate	HC14HSO4
$\text{H}_{25}\text{C}_{12}-\text{N}^+\text{H}_2-\text{SO}_4^-$	Di(dodecyldimethylammonium) sulfate	HC12SO4
16 carbon atoms (C16)		
$\text{H}_{33}\text{C}_{16}-\text{N}^+\text{H}_2-\text{HSO}_4^-$	Hexadecyldimethylammonium bisulfate	HC16HSO4
$\text{H}_{33}\text{C}_{16}-\text{N}^+\text{H}_2-\text{SO}_4^-$	Di(hexadecyldimethylammonium) sulfate	HC16SO4

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The protic (alkyldimethylammonium) bisulfate and sulfate ionic liquid precursors were synthesised in a thermostated reactor equipped with a magnetic stirrer. 0.01 mole of respective alkyltrimethylamine was dissolved in 20 ml of methanol. An appropriate amount of sulfuric acid was added portionwise in the next synthesis step. The whole mixture was stirred for 30 minutes (in case of sulfate liquid precursor until obtaining pH = 7), after which the mixture was evaporated, and the product obtained was dried in a vacuum dryer at 40°C for 36 hours.

The studies involved the use of lead powder produced using the Barton reactor by Linklater intended for ongoing battery manufacturing in AUTOPART. Firstly, the lead powder was subjected to physicochemical tests. The phase composition was determined by means of X-ray diffraction using Philips PW1050 equipment (CuK $\alpha$  radiation and Ni filter). The peak areas on the diffraction pattern were used to determine the relative content of ingredients: Pb 24.0%,  $\alpha$ -PbO 71.4% and  $\beta$ -PbO 4.6% (% relative). The powder was analysed granulometrically in the range of 0.05-878.67  $\mu$ m with Mastersizer by Malvern. The granulometric distribution is presented in Figure 1.

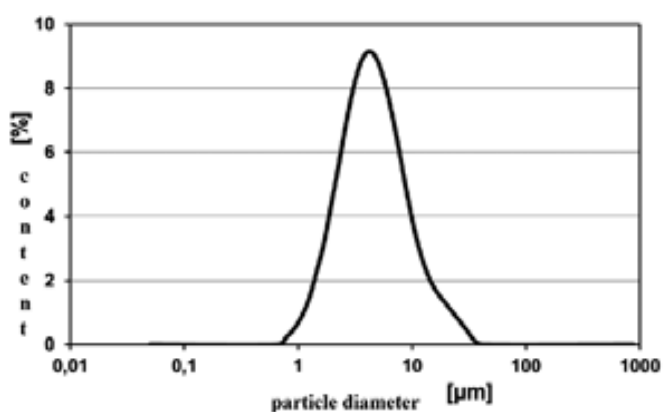


Fig. 1. Lead dust granulation

The results above lead to a conclusion that this is a powder with parameters allowing its use in manufacturing of the electroactive material for the lead-acid battery. In the next step, the same sample in the form of powder was tested by means of "reactivity at pH=4". This method involved adding a weighed amount ( $29.0 \pm 0.1$  g) of lead powder to 125 ml of 0.25 mole sulfuric acid solution containing the ionic liquid precursor (at a concentration of 5 mg IL in 1 cm<sup>3</sup> of the acid solution) and stirring the system at 500 rpm. A glass electrode Elmetron EPS-1 (pH measurement range 0-14) was immersed in the solution in order to analyse the changes in the pH. Time till reaching pH=4 by the system was measured, the measurement accuracy was 0.1 s; the results were averaged from 5 measurements. The results obtained were correlated with the values of conductivity for 1% solutions of ionic liquid precursors in water. Electrolytic conductivity was measured using a conductometric method. The conductometric electrode Elmetron EC 60 was used (electrolytic conductivity measurement range was 0.001-100 mS cm<sup>-1</sup>). Conductivity values were averaged from 3 measurements.

## Results

The effect of the structure of ionic liquid precursors on the rate of the reaction with lead powder and electrolytic conductivity of 1% IL solutions in water are presented in Table 2. The relative changes of reaction time (value 100% – pure 0.25 M sulfuric acid) with lead powder as a function of chain length are shown in Figure 2a, whereas Figure 2b shows the relative changes of reaction time (value 100% – pure 0.25 M sulfuric acid) with lead powder as a function of electrolytic conductivity of respective 1% ionic liquid precursor aqueous solutions.

Table 2

Ionic liquid precursors with lead powder average reaction times and conductivity of 1% ionic liquid precursors aqueous solution

Ionic liquid precursor	Reaction time with lead powder to the pH=4 s	Electrolytic conductivity of 1% solution mS cm <sup>-1</sup>
HC6HSO <sub>4</sub>	914.1	10.03
HC6SO <sub>4</sub>	937.0	6.65
HC14HSO <sub>4</sub>	817.4	7.09
HC12SO <sub>4</sub>	767.0	2.64
HC16HSO <sub>4</sub>	777.7	5.79
HC16SO <sub>4</sub>	722.4	0.19
H <sub>2</sub> SO <sub>4</sub>	843.4 <sup>1)</sup>	50.41 <sup>2)</sup>

<sup>1)</sup> 0.25 M sulfuric acid without ionic liquid precursor

<sup>2)</sup> 1% aqueous solution of sulfuric acid in water

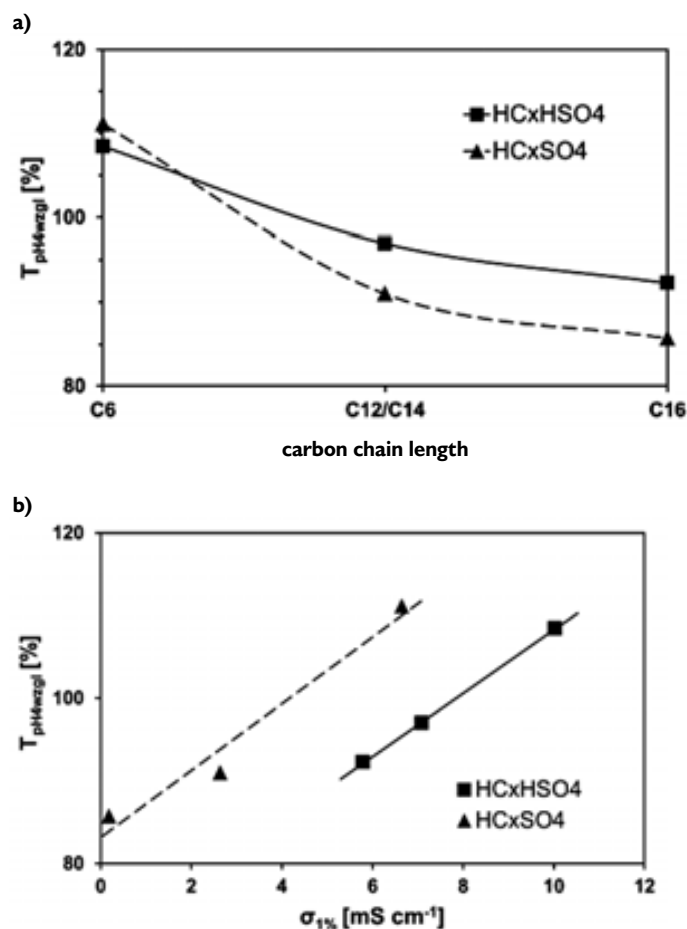


Fig. 2. (a) Relationship between relative reaction time ( $T_{\text{pH}4\text{wzgl}}$ ) and carbon chain for proton bisulfate ( $\text{HCxHSO}_4$ ) and sulfate ( $\text{HCxSO}_4$ ) ionic liquid precursors (b) relationship of  $T_{\text{pH}4\text{wzgl}} = f(\sigma_{1\%})$  for proton bisulfate ( $\text{HCxHSO}_4$ ) and sulfate ( $\text{HCxSO}_4$ ) ionic liquid precursors

Trend lines, equations and its coefficients were determined (Tab. 3) using Microsoft Excel<sup>®</sup>.

Table 3

Trend line equation and determination coefficient

Group of compounds	Linear regression equation	Coefficient of determination
HCxHSO <sub>4</sub>	$y = 3.83x + 69.96$	$R^2 = 0.9997$
HCxSO <sub>4</sub>	$y = 4.04x + 83.17$	$R^2 = 0.9656$

The trend line equations determined have high coefficients of determination, which indicates a good fit of model to the experimental data.

## Summary

The conducted studies on the relation between the structure of ionic liquid precursors and the reaction rate with lead power have shown that there is an effect of the type of the anion used and the length of the substituent at a nitrogen atom. Ionic liquid precursors with a cation with a shorter carbon chain had longer reaction times with lead powder. Moreover, sulfate ionic liquid precursors are better reagents than bisulfate ionic liquid precursors. This is caused by a presence of an easily dissociating proton in the acid radical. There was a strong relation between the electrolytic conductivity of ionic liquid precursor solutions and their rate of reaction. It came as a surprise that the higher the electrolytical conductivity of ionic liquid precursor solution was, the longer reaction time of a given IL with Pb/PbO was measured.

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## Aktualności z firm

### News from the Companies

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#### Koncern LANXESS w światowym indeksie Dow Jones

Od 19 września 2016 r. producent specjalistycznych środków chemicznych, koncern LANXESS, po raz szósty z rzędu znajdzie się w światowym indeksie zrównoważonego rozwoju Dow Jones (DJSI). Skład tego znanego na całym świecie indeksu zrównoważonego rozwoju określany jest raz do roku na podstawie czynników środowiskowych, społecznych i związanych z ładem korporacyjnym o istotnym znaczeniu finansowym. Przy określaniu firm, które zostaną ujęte w indeksie, stosuje się zasadę wybierania najlepszych podmiotów w danej klasie. Oznacza to, że tylko 10% ocenianych spółek z każdej branży zostaje włączone do indeksu DJSI World. W tym roku koncernowi LANXESS przyznano szczególne wyróżnienie za wyniki w dziedzinie procesów zarządzania innowacjami oraz strategii klimatycznej.

– *Bardzo cieszymy się z tego, że ponownie znaleźliśmy się w indeksie. Jest to dla nas potwierdzenie naszego zaangażowania w dziedzinie zrównoważonego rozwoju. Zrównoważony sukces ekonomiczny nie jest dzisiaj możliwy bez odpowiedzialnego podejścia do środowiska i społeczeństwa. Naczelna zasada zrównoważonego rozwoju jest silnie zakorzeniona w naszej korporacyjnej strategii – podkreślił Hubert Fink, członek Zarządu.*

Indeks DJSI sporządzany jest przez S&P Dow Jones Indices, jedne z najważniejszych na świecie podmiotów oferujących indeksy rynków finansowych, we współpracy z RobecoSAM, spółką zarządzającą aktywami specjalizującą się w dziedzinie zrównoważonego inwestowania. W tym roku do udziału w ocenie zaproszono 3.400 największych na świecie spółek z krajów rozwiniętych i rozwijających się.

Więcej informacji na temat inicjatyw koncernu LANXESS w dziedzinie społecznej odpowiedzialności przedsiębiorstw: responsibility.lanxess.com. (abc)

(inf. LANXESS, 12 września 2016)