Lead oxide battery grade synthesis via formation and decomposition of lead citrate

Conference Paper · June 2015

DOI: 10.13140/RG.2.2.13218.63688

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Abstract

In this study, as part of developing a new process which can avoid smelting and electro-winning, leaching was used for dissolution of waste lead paste in order to produce firstly lead citrate. Leaching experiments were performed in laboratory conditions in 1 L-glass reactor. Scale up of leaching was investigated in 200 L- reactor. The thermal decomposition of prepared lead citrate was performed in neutral and oxidizing atmosphere between 280°C and 340°C in 60 min in order to produce lead oxide. DTA and TGA analysis were shown that dehydration was virtually complete before thermal decomposition. Optimal thermal decomposition conditions were determined by investigating the effect of flow rate and type of protective atmosphere. Different solid products were produced depending on the reaction conditions.

1 Introduction

Lead-acid batteries are widely used for storage in backup power supplies in cell phone towers, high-availability settings like hospitals, and stand-alone power systems. In most of the applications where lead is used, especially lead-based batteries, it is possible to recover metals for use over and over again without any loss in quality [1]. Furthermore, as all lead-based batteries have the same basic chemistry, this means that all types of lead battery can be processed easily by lead smelters. Nowdays, there has been a continuing interest in improving the electrode active material quality in lead-acid storage batteries to increase energy efficiency and decrease of operational costs for recycling. Mahato and Laird [2] have studied various additives, commonly referred to as expanders, which have been used particularly in the paste for making negative battery plates. It is known that expanders improve the efficiency of utilization of the active materials, particularly, the high rate, low temperature discharge capacity and the operational life of the battery. But, in last time the recycling of lead paste from lead acid batteries is main focus of different studies. Two ISASMELT^{TM} plants [2] have been constructed to date for recycling lead batteries, producing fine lead and a low-lead silicate slag. Smelting and using iron (Fe) to ‘fix’ the sulphur component also generates a hazardous FeS-PbS matte. Furthermore, alternative processes using short-rotary furnaces, hydrometallurgy and electro-winning have their own share of toxic by-products, and are capital and energy intensive.

Kumar [3] has developed new strategies for recycling of lead-acid batteries and patented such that precursors for battery plates are directly produced in an environmentally sound process that is sustainable with respect to both materials and energy. The method reduces energy consumption as well as carbon and sulphur dioxide emissions, compared to existing approaches. His team has extracted lead from spent batteries used in vehicles, back-up telecommunication facilities and power generating stations by reacting active lead sulphate ($PbSO_4$) paste in a non-hazardous aqueous solution [4]. The chemicals used are organic reagents such as carboxylic acid and salts. The paste is decomposed to produce a sodium sulphate by-product, while lead is crystallized into an organic precursor. Once subjected to combustion-calcination at 350ºC, lead oxide (PbO) granules are generated for reuse in battery manufacture. Kumar reported that an availability of a sustainable technology will increase incentives for advanced lead batteries that can deliver much higher energy and power densities for electrical vehicle applications. Zhu et l. [7] prepared the lead citrate precursor, $Pb(C_6H_6O_7)\cdot H_2O$, by leaching desulfurized paste with citric acid and H_2O_2. Ultra-fine PbO/Pb powder with particle size of 100–500 nm was obtained at 370 °C after thermal decomposition of lead citrate.

The aim of this study was synthesis of lead citrate from waste lead paste and especially to test scale up of leaching process in order to produce 10 kg of lead citrate. Thermal decomposition of prepared lead citrate was investigated in different protective atmospheres in order to produce lead oxide preventing a formation of undesired lead in molten state.

2 Experimental work

2.1 Fundamental background of lead citrate formation and decomposition

Generally, the thermal decomposition of metal carboxylates in oxidizing atmospheres leads to formation of the metal oxides, carbon dioxide (carbon monoxide) and water vapor. In inert atmospheres, however, the solid products may be the metal and /or the metal carbide and possible some carbon. For lead carboxylates, the formation of metal rather than PbO is thermodynamically favored, although a mixture of PbO and Pb is reported as the product of the thermal decomposition of lead oxalate. Brown [5] proposed the stoichiometry of the decomposition of lead citrate, after initial dehydration steps:

$$Pb_3(C_6H_5O_7)_2 \text{ (s)} = [3 \text{ Pb} + 7.5 \text{ C}] + 5 \text{ } H_2O \text{ (g)} + 4.5 \text{ } CO_2 \text{ (g)} \qquad (1)$$

Therefore an influence of different protective atmospheres in order to control the final solid products was studied.

2.2 Material

The investigated paste scrap from an industrial beneficiation plant is shown at Figure 1. Moisture contents amounts between 6 and 7 wt. % in a tested paste scrap. Free lead content determined by wet chemistry is about 32 wt %. Phase composition of lead compounds was determined using XRD-analysis and presented in Table 1 and in Figure 1:

Table 1: Phase composition of the lead paste scrap

Lead compounds	Mean composition (Wt. % in dry sample)	 Figure 1: Lead Paste Scrap
Pb	32	
α–PbO	1.2	
4 $PbO \cdot PbSO_4$	3.0	
$PbO \cdot PbSO_4 \cdot H_2O$	13	
$PbSO_4$	27.8	
2 $PbCO_3 \cdot Pb(OH)_2$	2.0	
α–PbO_2	7.5	
β–PbO_2	12	

XRD-Analysis was performed using a sieved lead bearing components. Limitation of XRD-analysis is that this method sees crystalline material (non-amorphous material). The accuracy of method amounts about 4 wt. %.

2.3 Leaching in laboratory conditions

The paste scrap is firstly dried over night at 70°C and dissolved in a 1 L glas reactor under an atmospheric pressure using citric acid, acetic acid and small additives of sodium hydroxide and hydrogen oxide. Temperature was controlled within ± 3 ^{o}C by a temperature control system, manipulating both a water cooling system (see Figure 1). Different fraction of sample were tested (about 500 µm). The sieving analysis was performed using Retsch system, Germany. Agitation was provided by an impeller that is motor driven. A certain amount of lead paste was mixed with a pre-calculated amount of deionised water. Then the slurry was heated up to a predeterminated temperature under continuous agitation. Upon temperature stabilisation, first sampling was performed. Precipitation follows the leaching process.

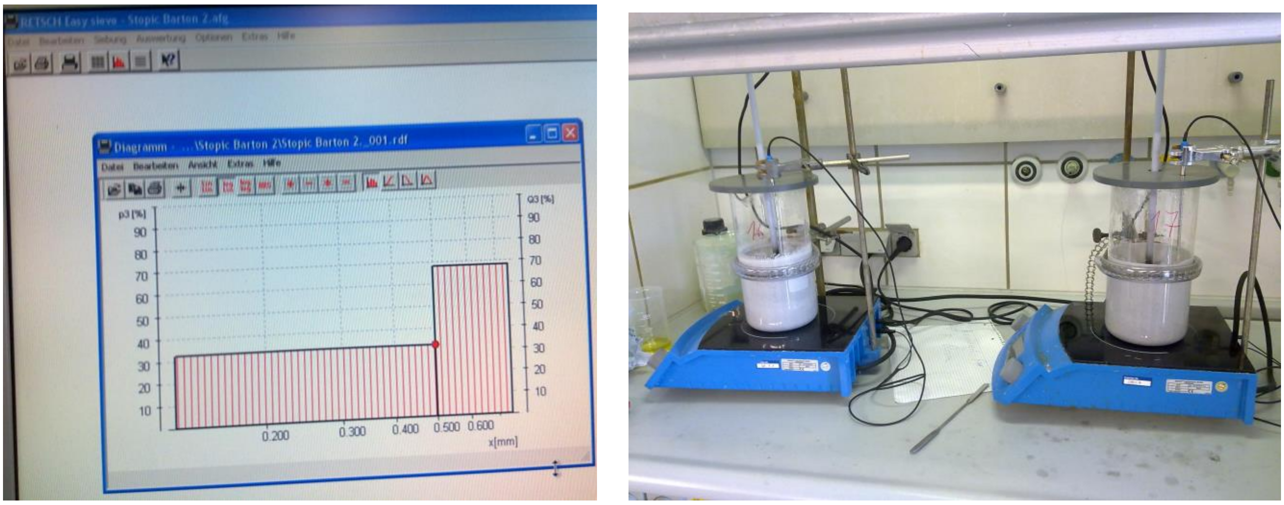

Figure 2: Grain size distribution of a chosen sample and our leaching equipment in laboratory

2.4. Scale up of leaching

After first investigation of optimal parameters in laboratory conditions in volume of 1 L, a similar procedure was tested in 200 L reactor, as shown at Fig. 3.

	Operating parameters: Reactor volume: 200 L First step: 30°C, 4 hours Second step: 50°C, 4 hour Sample: 15 kg (fraction under 500 µm) Operating Solution: 150 L Solution components: water, sodium hydroxide, citric acid monohydrate, acetic acid, hydrogen peroxide Overnight above 32 °C (16 hours) Solid product after filtration: 10 kg

Figure 3: Leaching in 200-L reactor and description of operating conditions

After drying and sieving the fraction under 500 µm was dissolved using appropriate quantities of citric acid, acetic acid, sodium hydroxide and hydrogen peroxide. The leaching experiments were performed in two heating steps: 1) firstly at 30°C in 4 hours, and 2) then in 50°C in 4 hours. An injection of protective gas took place over the night above 32°C. After filtration and drying the obtained lead citrate is shown in Fig. 4. SEM analysis of lead citrate has shown the partially agglomerated round and irregular particles.

Figure 4: Produced lead citrate in 200 L reactor with a typical SEM image of a filter cake

2.5. Thermal decomposition of lead citrate to battery grade lead oxide

Decomposition of lead citrate was investigated in non-isothermal and isothermal conditions. DTA and TGA analysis is shown at Figure 5.

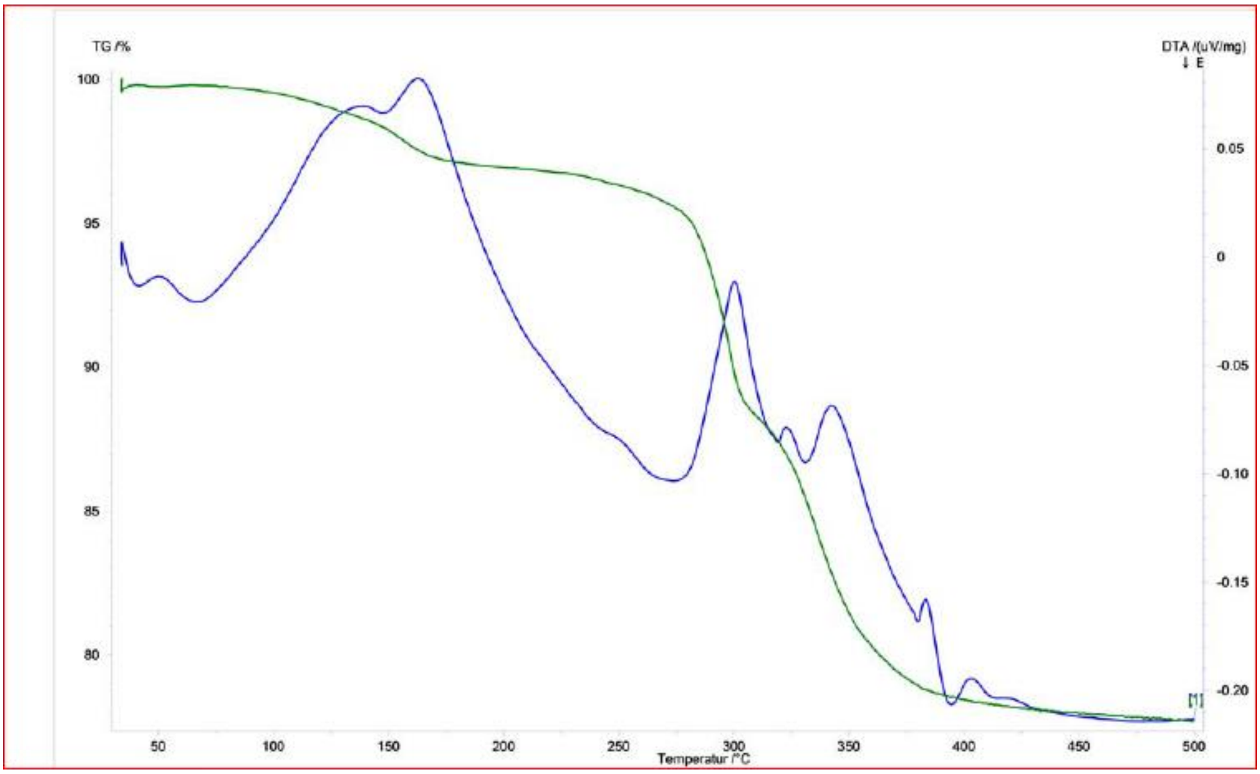

Figure 5: DTA/TGA analysis of thermal decomposition of lead citrate in argon

As shown at Figure 5 the thermal decomposition of lead citrate in inert atmosphere takes place in two main stages: dehydration of water and formation of metallic phases and gaseous phase. The experiments were performed below the melting point of lead in order to prevent formation of molten lead, which is undesired product for this thermal decomposition.

Thermal decomposition was performed in rotary furnace using parameters presented in Table 2.

Table 2: Decomposition of lead citrate (heating rate 25 K/min, residence time 60 min)

Experiment	1	2	3	4	5
Gas	N_2	Air	Air/H_2O	N_2/Air	N_2/Air
Flow rate (l/min)	3	3	3/4	1.5/1.5	1.5/1.5
Temperature (°C)	310 (max 340)	310 (max 340)	310 (max.340)	310 (max.340)	280 (max 320)

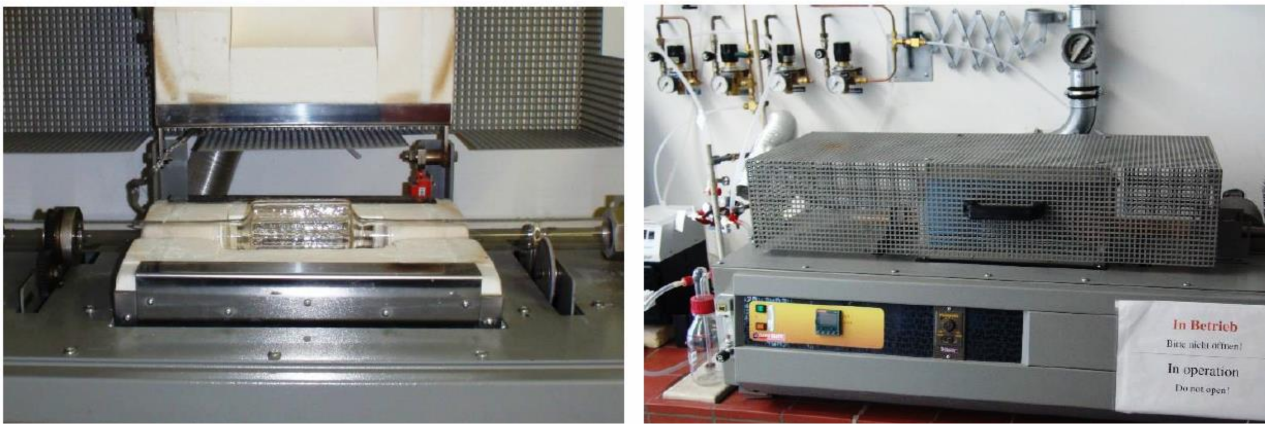

Figure 6: Carbolite rotary furnace used for thermal decomposition of lead citrate

Generally, during this decomposition process the next phases were formed: main phase β-PbO; and intermediate phase: α-PbO, metallic Pb and Lead oxide hydrate (only present in nitrogen atmosphere). It was detected by XRD-analysis (as shown in Figure 7).

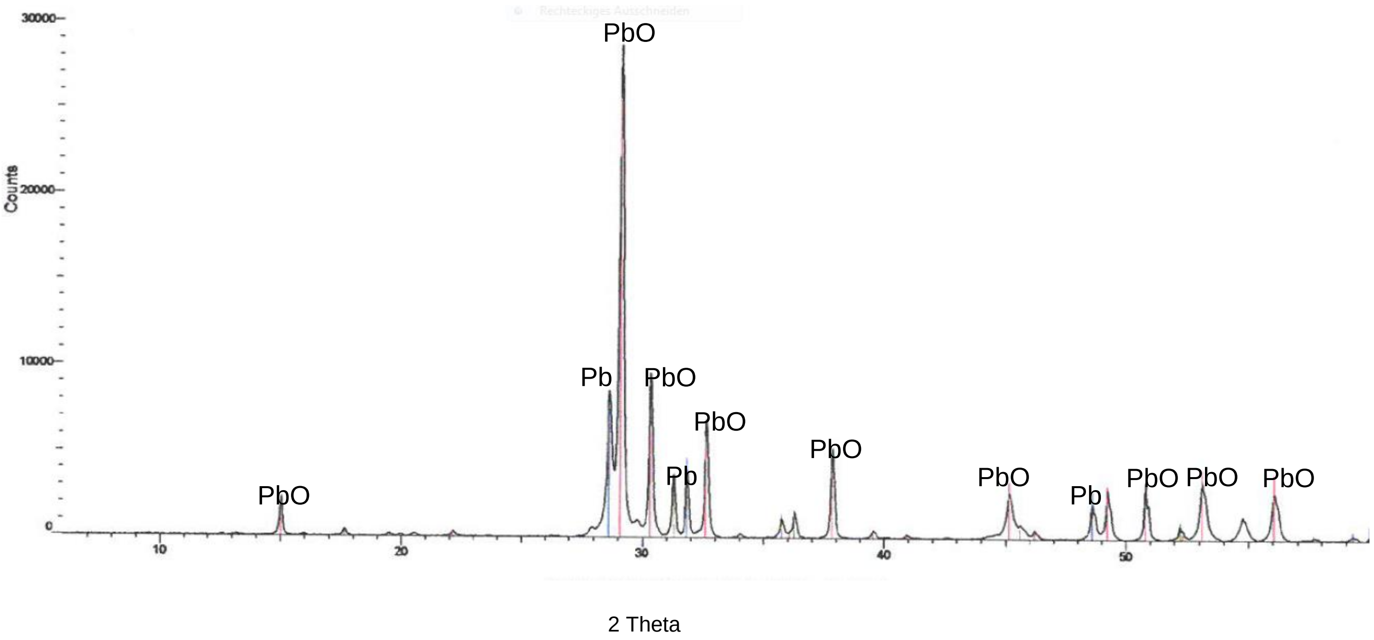

Figure 7: XRD-analysis of powder obtained in nitrogen/air atmosphere at 310°C (Exp.4)

3. Conclusion

In this study, a new process for the synthesis of lead oxide battery grade via formation and decomposition of lead citrate from paste scrap using drying, sieving, leaching, precipitation, filtration, and final thermal decomposition was successfully applied. Leaching experiments were firstly performed in laboratory conditions in 1 L reactor using citric acid with some additives from acetic acid, sodium hydroxide and hydrogen peroxide. Then using same procedure during scale up of leaching process, the operating parameters were tested in 200 L reactor. The thermal decomposition of prepared lead citrate was investigated in non-isothermal conditions (DTA and TGA analysis) and then in a rotary furnace in isothermal conditions in order to test different protective atmospheres for formation of lead oxide. During this process the next phases were formed: main phase: β-PbO, and intermediate phase: α-PbO, metallic Pb and Lead oxide hydrate (only present in nitrogen atmosphere). The next steps shall be focused in order to study the kinetics of lead oxide formation from lead citrate.

4 References

[1] http://www.eurobat.org/eurobat-and-acem-call-further-support-electrification-l-vehicles-20-november-2013

[2] Mahato, B. K and Laird, E. C (1982): Battery paste for lead-acid storage batteries, US Patent 4323470 A

[3] www.isasmelt.com/ISASMELT FOR LEAD RECYCLING.pdf

[4] Kumar, RV, Sonmez, S & VP Kotzeva, VP (2006): "Lead Recycling" British Patent Application 2006, GB0622249.1; PCT Application No. PCT/GB2007/004222.

[5] http://www.iom3.org/news/lead-paste-recycling?c=574

[6] Brown, M.E (1973): Thermal decomposition of Lead Citrate, J.Chem.Soc. Faraday Trans. 1, 69, 1202-1212.

[7] Zhu, X, Lei, L., Sun, X, Yang, D., Gao, L., Liu, J., Kumar, RV, Yang, J (2012): Preparation of basic lead oxide from spent lead acid battery paste via chemical conversion, Hydrometallurgy, 117-118, 24-31.