



FEDERAL REPUBLIC OF NIGERIA
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RP:NG/PT/NC/2017/2459

Date of Patent: 19/10/2017

Date of Sealing: 10/08/2018

President of the Federal Republic of Nigeria and commander-in-Chief of the armed forces
MUHAMMADU BUHARI, GCFR

Whereas a request for the grant of a patent has been made by: **DR. MARY B. OGUNDIRAN, MR TOPE D. OGUNDELE and DR. MANIS K. JHA** of **ANALYTICAL/ENVIRONMENTAL UNIT, DEPARTMENT OF CHEMISTRY UNIVERSITY OF IBADAN, OYO STATE, NIGERIA, ANALYTICAL/ENVIRONMENTAL UNIT, DEPARTMENT OF CHEMISTRY UNIVERSITY OF IBADAN, OYO STATE, NIGERIA and METAL EXTRACTION AND FORMING DIVISION, CSIR- NATIONAL METALLURGICAL LABORATORY JAMSHEDPUR, INDIA, C/O DR. RAPHAEL ADEOLUWA, ADERAPH SOLICITORS of 1ST FLOORR, NO.31 OGUNMOLA STREET, VINE STORE BUS STOP, ASI-BODIJA WAY, IBADAN, OYO STATE, NIGERIA.**

For the sole use and the advantage of an invention for: **A PROCESS FOR PRODUCTION OF NANO-PbO FROM SPENT AUTOMOBILE LEAD-ACID BATTERY.**

AND WHEREAS the Federal Government being willing to encourage all invention which may be for the public good, is please to accede to the request:

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MADE this date: 10th day of August, 2018



STELLA OZO EZENDUKA
 Registrar

Title of Patent: A process for production of nano-PbO from spent automobile lead-acid battery

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Abstract

The present invention provides an improved process for synthesis of lead organic compound from spent automobile lead-acid battery as precursor for production of nano-PbO. In the method, a survey of lead-acid battery types in South-Western Nigeria is made and spent lead-acid batteries are collected. The batteries are dismantled and the paste therefrom, which contains PbSO₄, Pb₃O₂SO₄, PbO₂, PbO and Pb is separated. The paste is slurred to test acidity, is screened to a particular particle size, and its lead components are simultaneously desulphurised, leached, reduced and precipitated as lead organic compound. The desulphurising and leaching solutions are first mixed, then the paste is added, and then the reducing agent. The precipitated lead precursor is subjected to calcination process to yield purified nano-structured lead (II) oxide (nano-PbO), which can be used to produce new automobile battery.

Field of the invention

The present invention relates to a process for production of nano-PbO from spent automobile lead-acid battery by a green chemical method and calcination.

Background of the invention

Lead acid batteries power a great number of automobile vehicles globally. When they are spent they can become important raw materials for producing electrodes of new lead-acid batteries. The growth in its demand creates the need to recycle the waste rather than disposal. Traditionally, pyrometallurgy (fusion-reduction method) has been a popular method of reducing all lead (Pb) compounds in the waste to metallic Pb by means of heating and reduction. The Pb bullion produced is refined to be applied for other purposes. In Nigeria and many developing countries, where environmental regulations and enforcement are weak, Pb is

extracted from spent Pb-acid batteries by crude open-air pyrometallurgical methods. This is different from what obtains in the developed countries where pyrometallurgical processes are practised in highly built-up plants. The drawbacks of the crude methods include usage of large amount of energy, high operational costs, emissions of Sulphur dioxide (SO_2), Pb particulate matter; and generation of Pb-containing drosses and slag which are dangerous to environment and human health. Through the crude pyrometallurgical methods, the recyclers, the local residents and environment are exposed to Pb contamination. Exposure to lead can cause health effects including damage to kidneys, central nervous system, cardiovascular system, reproductive system and neurological development in children. Therefore, there is a need to develop green and adaptable method for recycling spent automobile lead-acid battery in both developing and developed countries.

Conventionally, PbO bulk crystals with particle size at micrometer levels have been used in the production of lead-acid battery electrodes. Lead oxide paste is generally used in lead-acid battery manufacturing as the initial active material for both anode and cathode of the battery. Presently, synthesis of nanometer dimensional PbO materials for application as electrodes in the production of new Pb-acid battery using hydrometallurgical methods is attracting attention. This is due to the improved particle size, large surface area, improved discharge capacities and other electronic properties of nano-PbO. Innovative processes have been published but industrial application is yet to gain ground. Existing hydrometallurgical methods either convert all lead compounds in the spent paste into metallic Pb and nano-PbO or only nano-PbO, but with some drawbacks in the methods.

According to U.S. Patent Number 4460442A in which hydrometallurgical method for recovering Pb from spent lead-acid storage batteries was reported. In the method, the spent pole active materials, which were mainly Pb and PbO_2 were separated, and reacted in the presence of a strong alkaline solution (NaOH and KOH) to yield a precipitate. The precipitate was subsequently solubilised with an appropriate acid and the solution was subjected to electrolysis to obtain Pb as the final product. The drawbacks of the method are that only the active poles (Pb and PbO_2) were separated and recycled. But PbSO_4 which also constituted a substantial proportion of the paste was not considered. In addition, the process is long and the final product cannot be applied directly in producing new battery.

According to the article "Synthesis of uniform nano-structured lead oxide by sonochemical method and its application as cathode and anode of lead-acid batteries" authored by H. Karami,

M. A. Karimi, S. Haghdar; *Materials Research Bulletin* 2008, Volume 43: pp 3054-3065 wherein lead carbonate was synthesised from reaction of lead nitrate and sodium carbonate solutions, and the precipitate was calcinated to produce nano-structured lead (II) oxide. The drawback of this process is that laboratory chemicals were used to synthesise n-PbO which may not be of industrial interest due to the cost and potential hazards of the inorganic chemicals involved.

According to the article “Leaching of waste battery paste components. Part 1: Lead citrate synthesis from PbO and PbO₂” authored by M.S. Sonmez, R.V. Kumar; *Hydrometallurgy* 2009, Volume 95: pp 53-60 and “Leaching of waste battery paste components. Part 2: leaching and desulphurisation of PbSO₄ by citric acid and sodium citrate solution”, authored by M.S. Sonmez, R.V. Kumar; *Hydrometallurgy* 2009, Volume 95: pp 82-86 in which simulated battery paste components, PbO, PbO₂ and PbSO₄ using laboratory chemicals were reacted with citric acid, its salt and hydrogen peroxide to synthesis nano-PbO. The drawback of this process is that simulated Pb-acid battery were used which may not signify what happens in the real life situation of spent Pb-acid battery paste. Also, PbO and PbO₂; and PbSO₄ were leached separately but they occurred together in the real life spent paste.

According to the article “Preparation of basic lead oxide from spent lead acid battery paste via chemical conversion”, authored by Zhu X., Li L., Sun X., Yang D., Gao L., Liu J., Kumar R. V., Yang J; *Hydrometallurgy* 2012 Volume 117-118 pp 24–31: where it is reported that real life spent Pb-acid battery paste was desulphurised first using inorganic salt solutions, then filtered, and the residue was treated with citric acid and hydrogen peroxide to produce lead citrate which was calcined to produce nano-PbO. The main drawback of this process is that desulphurisation, leaching, reduction and precipitation were performed by two distinct processes which increased the time of production of nano-PbO from the paste in addition to evolution of CO₂ during the reaction.

According to the article “Preparation and characterisation of nano-structured lead oxide from spent lead acid battery paste”, authored by Li L., Zhua X., Yanga D., Gao L., Liu J., Kumar R. V., Yang J; *Journal of Hazardous Materials* 2012 Volume 203-204: pp 274-282, where it is reported that real life spent Pb-acid battery paste was leached with citric acid, its salt and hydrogen peroxide using optimised conditions reported previously, combusting the Pb citrate obtained in nitrogen and air. The phase transformation of the precursor after calcination showed

the presence of Pb metal in the final products (Pb, litharge α -PbO and massicot- β -PbO). Some carbon was also identified in the calcination product. The drawbacks are (i) the synthesis parameters were not directly optimised on the real life spent paste. This may lead to low solubility of chemical components of the paste by the citric acid and hydrogen peroxide. Besides, ineffective desulphurisation by the sodium citrate solution may also occur. (ii) The presence of Pb and C in the final product may be disadvantageous for making new electrodes. In the present study, the spent Pb-acid batteries used were collected from locals and characterised for uniformity of composition. The proposed method converts all Pb compounds directly into carbon-free, high purity nano-PbO which can be used directly in the production of new batteries.

Object of Invention

The general goal of this invention is to provide an optimised process to produce high purity nano-structured PbO from spent Pb-acid battery paste from Nigeria using hydrometallurgical process and calcination that exclude the drawbacks of the existing methods, and can be industrially adapted both in the developing and developed countries.

Another object of the invention is to develop a process with reduced energy requirement, which eliminates emission of gasses and generation of Pb contaminated wastes. It is another object of the invention to develop a simple, fast, more convenient, less expensive method wherein desulphurisation, leaching, reduction of the paste components and precipitation of Pb occur simultaneously with maximum recovery efficiency of Pb from the paste.

Yet another object of the invention is to optimise lead oxide precursor synthesis conditions for improved desulphurisation, leaching, reduction, and precipitation reactions. It is another object of the invention to provide the temperature at which nano-PbO precursor loses its organic content and forms a stable product. Another object of the invention is to calcinate the precursor at the selected temperature to produce nano-PbO as the final product.

Statement of invention

This invention relates to a process wherein iron, carbon and sulphur-free nano-PbO powder with particle size of 60-300nm is produced from concurrent leaching, desulphurisation, reduction and precipitation of the whole content of locally sourced automobile lead-acid battery

paste including PbSO_4 , PbO_2 , residual PbO , Pb and $\text{Pb}_3\text{O}_2\text{SO}_4$, with mixing order, citric acid, sodium citrate, paste and then hydrogen peroxide.

Summary of the invention

In this invention, composition of spent lead-acid battery from Nigeria and a novel, fast, energy efficient, cost-effective, simple and high recovery efficient hydrometallurgical process to synthesise lead organic compound from spent Pb-acid battery as precursor for production of nano-PbO which overcomes some of the drawbacks of the existing methods as discussed above, is provided.

In a preferred embodiment, a process for producing nano-PbO from spent automobile lead-acid battery pastes is carried out by first sourcing for locally available spent Pb-acid batteries, then dismantling them to separate the paste and providing information about its composition.

In another embodiment, the process for producing nano-PbO from spent automobile lead-acid battery pastes may further include the step of screening the paste into a single particle size and slurring in water to test for residual acidity level. The process may again include solubilisation of the paste in inorganic acid solutions to obtain the total concentration of Pb and other metals in the paste.

The process may further include treating the dried paste with different organic acids, their salts and hydrogen peroxide at different concentrations, mixing ratios and mixing sequence, for maximum recovery of Pb from the paste prior to selection of appropriate leaching, desulphurising, reducing and precipitating agents for synthesis of precursor for nano-PbO production. Additionally, the process may include the step of filtering and rinsing the precursor precipitates formed and measuring the non-precipitated Pb in the filtrate.

In another embodiment, the present invention provides a process for preparing nano-PbO precursor including the steps of optimising the concentration of organic acid, paste/solution ratio, reaction temperature, stirring speed and reaction time for the selected leaching, desulphurising, reducing and precipitating agents. These conditions will ensure improved solubility and effective desulphurisation of chemical components of the paste for the synthesis of nano-PbO precursor. On completion of each experiment, the process may further include vacuum filtration of the precipitates and measurement of the non-precipitated Pb in the filtrate.

The current invention is further directed towards using the effective conditions to synthesis Pb precursor. In yet another embodiment, the present invention provides a process for preparing

nano-PbO from the precursor, which involves thermal analyses to determine the exact temperature at which the precursor loses its organic content and forms a stable product. The process may further include the step of calcinating the precursor at the selected temperature to obtain nano-PbO as the final product.

Brief description of Drawings

The process of this invention provides composition for spent lead-acid battery from Nigeria and simultaneous leaching, desulphurisation, reduction and precipitation for recovery of Pb from real life spent Pb-acid battery in form of nano-PbO which were not quite described in literature. This may be summarised by the following flow charts.

The processes of providing spent Pb-acid battery, dismantling and component separation; selecting appropriate leaching, desulphurising, reducing and precipitating agents are shown in Figure 1.

The processes for selection of reaction conditions for the selected leaching, desulphurisation, reducing and precipitating reagents are shown in Figure 2.

The processes for synthesis of lead precursors from waste automobile lead-acid battery paste for production of high purity nano-lead (II) oxide using the optimised reaction conditions for the selected leaching, desulphurisation, reducing and precipitating reagents are shown in Figure 3.

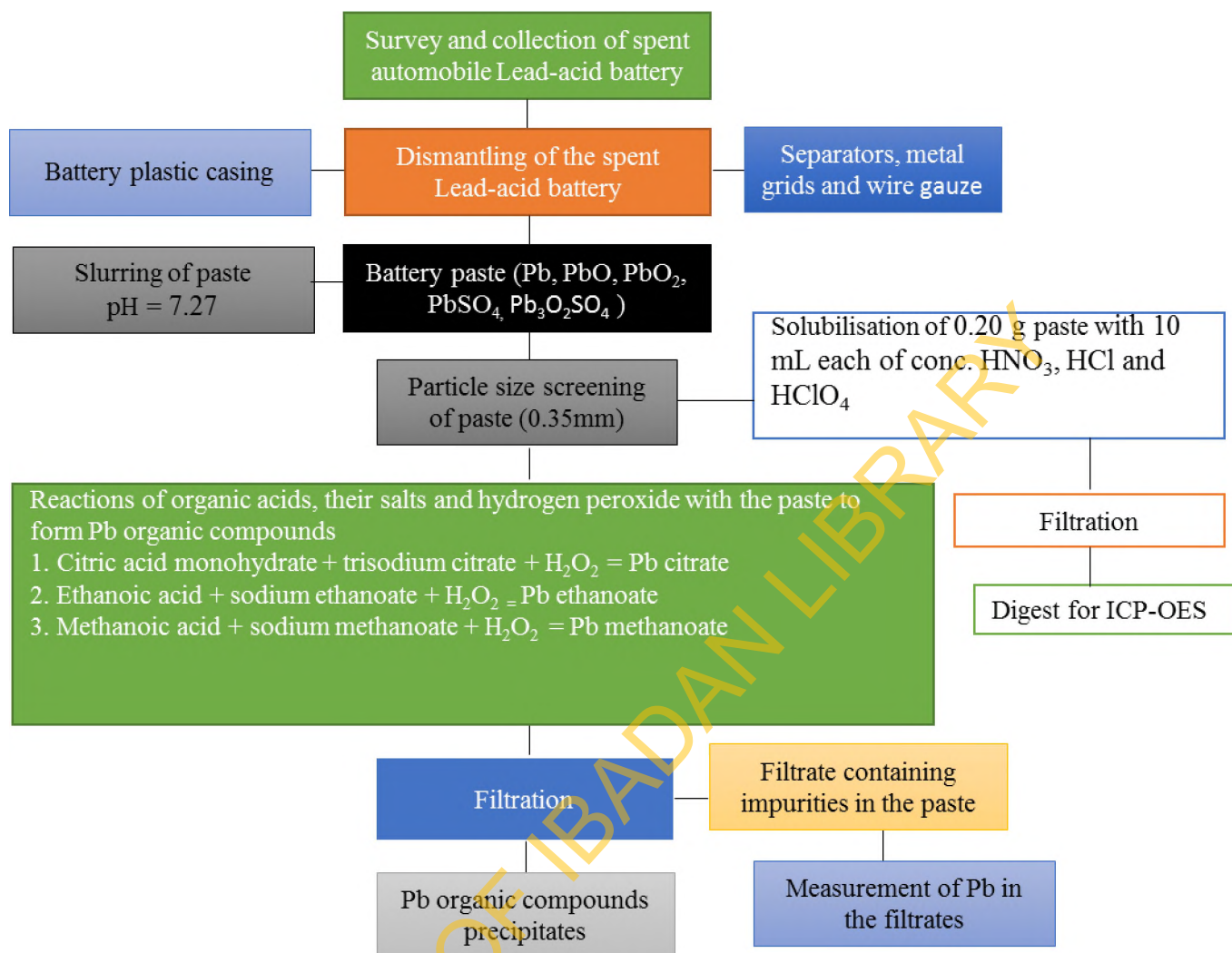


Figure 1 shows the processes for collection of spent lead-acid batteries, discharging, dismantling, paste pre-treatment, digestion of the paste, and selection of appropriate leaching, desulphurisation, reducing and precipitating agents.

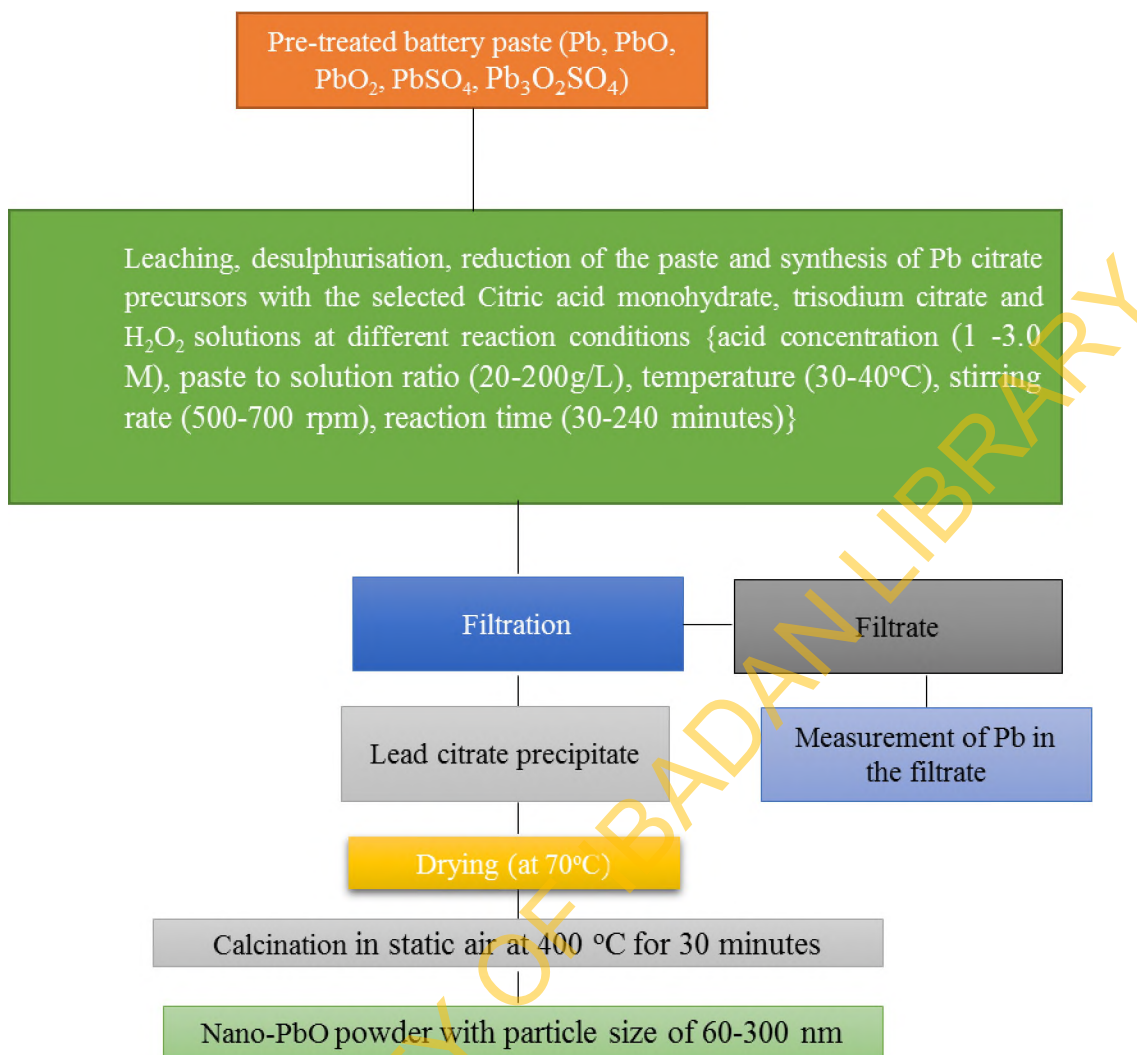


Figure 2 shows the processes for selection of optimal conditions for the selected leaching, desulphurisation, reducing and precipitating reagents.



Figure 3 shows the processes for synthesis of lead precursors from waste automobile lead-acid battery for production of high purity nano-lead (II) oxide using the optimised parameters for the selected leaching, desulphurising, reducing and precipitating reagents.

Detailed summary of the invention

Basically, the invention is about production of lead citrate from spent lead-acid battery paste which is simply transformed to nano-lead (II) oxide by calcination. The present invention will henceforth be described fully with references to the accompanying processes in which some examples of the embodiments of the invention are shown. An improved procedure for forming nano-lead (II) oxide from spent lead-acid battery paste includes collection of spent lead-acid battery from the locals, dismantling and separation of components, solubilisation of total Pb and other metals in the paste, simultaneous reduction of lead (IV) oxide with hydrogen peroxide, desulphurisation of lead sulphates with organic acid salts, leaching of metallic Pb and residual lead (II) oxide with organic acids, precipitation of leached lead with anions of the acids, subsequently, filtering, washing of the precipitate, drying and calcination of lead organic precursor. In this process, sulphate ions, metal impurities and unreacted Pb, if any, are contained in the filtrate. The stage by stage description of the process is given with reference to Figures 1, 2, and 3.

The examples below are given to illustrate the functioning of the invention in practice. In actual fact, this invention may be embodied in many different forms and should not be interpreted as limited to the embodiments described here.

Example 1: Spent lead-acid battery collection and pre-treatment

A survey of spent lead-acid battery types in South-Western Nigeria is made and spent lead-acid batteries are collected based on the similarity of types. The batteries having established the state of discharge by touching the terminals of the batteries with electrical wire, are dismantled and the paste which contains lead (II) sulphate (PbSO_4), lead (IV) oxide (PbO_2), residual lead (II) oxide (PbO), lead metal (Pb) and $\text{Pb}_3\text{O}_2\text{SO}_4$ are separated. The paste is slurred in 70°C water for 1 hour on a magnetic stirrer operated at 450 rpm on a hot plate to ascertain neutrality. The paste is homogenised by screening to 0.35 mm using scientific sieve of mesh size 48 on a mechanical shaker.

Example 2: Solubilisation of metals in the paste

The composite paste is prepared by taking 2g each of the 50 spent lead-acid battery paste samples, homogenised and digested. This is done by digesting 0.20 g of the sample with 10 mL each of conc. HNO_3 , HCl and HClO_4 using micro wave digestion system. After the dissolution, the digested sample is filtered into 250 mL standard flask and made up to the mark with distilled water and Pb, Cd, Ag, As, Co, Cr, Cu, Fe, Mn, Ni, Sb, Se, and Te are determined in the digest with inductively coupled plasma optical emission spectrophotometer.

Example 3: Selection of paste leaching/desulphurisation/reduction/precipitation system

The lead components of the paste are leached, desulphurised, reduced and precipitated as lead organic compounds using three different low molecular weight carboxylic acids {Methanoic acid, ethanoic acid and citric acid (1,2,3-tricarboxylic acid)}, their salts (sodium methanoate, sodium ethanoate and sodium citrate) and 30% hydrogen peroxide solutions with concentrations ranging from 1-2 M maintained at pH 3.9. Each of the combined solutions are mixed together with the paste in a temperature-controlled, closed, three-necked Pyrex flask glass reactor either as the three solutions combined before the addition of the paste or as the acids and their salts solutions combined, then addition of paste follows by the addition of hydrogen peroxide. The ratio of the paste to the solution is 1:10. The reaction mixtures are kept stirred at room temperature for a period of 30 minutes to obtain Pb precipitate precursors. When the reaction is complete, the precipitate is separated by vacuum filter and the filtrate collected for analyses to determine unreacted Pb. Operating by the latter option of the addition of reactants, the viscosity of the slurry is reduced and precipitation is enhanced. In actual fact, the amounts of lead precipitated are much more going by this option. As an illustration, 10 g of spent lead-acid battery paste is leached, desulphurised and reduced by 100 mL each of the three

types of systems: (1) 1M citric acid, 2 M trisodium citrate and 2M 30% hydrogen peroxide (2) 1M ethanoic acid, 2M sodium ethanoate, and 2M 30% hydrogen peroxide; and (3) 1M methanoic acid, 2M sodium methanoate and 2M 30% hydrogen peroxide in the ratio 2:1:2 respectively. The 1M citric acid, 2 M sodium citrate, 2M hydrogen peroxide with mixing sequence of citric acid and sodium citrate first followed by paste and then hydrogen peroxide performs best.

Example 4: Reaction conditions of the selected desulphurisation, leaching, reducing and precipitating system

In another embodiment of the method, according to this invention, wherein it is desired to improve the selected desulphurisation, leaching, reducing and precipitating system to enhance precipitation of lead citrate precursor. The paste is subjected to leaching, desulphurisation, reduction and precipitation at different concentrations of citric acid solution (1 -3.0 M), paste to solution ratio (20-200g/L), temperatures (30-40°C), stirring rate (500-700 rpm), reaction time (30-240 minutes) with mixture of citric acid and sodium citrate solutions first followed by the addition of the paste, then hydrogen peroxide. It is found that 1M citric acid, 2 M sodium citrate, 2M hydrogen peroxide, 100 g/L paste to solution ratio, 30 °C temperature, 500 rpm stirring rate and 3 hours reaction time are suitable for simultaneous leaching, desulphurisation and reduction of the paste to precipitate lead citrate precursor.

Example 5: Synthesis of Pb citrate precursor and production of nano-PbO

100g of spent lead acid battery paste is leached at 30°C with 1 L mixture of 1M citric acid, 2 M sodium citrate, 2M hydrogen peroxide (2:1:2), at pH of 3.94 in sequence as above, the mixture is stirred at 500rpm in a closed, three-necked Pyrex flask glass reactor using magnetic stirrer for 3 hours. Within 3 hours the brownish spent paste turns to whitish precipitate. When the reaction is complete, the precipitate is separated through vacuum filter, washed with water, dried at 70°C. The filtrate contains unreacted Pb and other metal impurities in the paste. The dried whitish precipitate is subjected to calcination in a platinum crucible in static air at 400 °C for 30 minutes at heating rate of 10 °C min⁻¹. The whitish lead citrate precursor changes to yellowish carbon and sulphur-free nano-PbO

It is hoped that the process which includes simultaneous leaching, desulphurisation, reduction of the battery paste at 1M citric acid, 2 M sodium citrate, 2M hydrogen peroxide (2:1:2) at pH 3.9, 100 g/L paste to solution ratio, 30 °C temperature, 500 rpm stirring rate and 3 hours reaction time and the precipitate dried at 70°C and calcination at 400 °C will be useful for

recycling of waste Pb-acid battery paste into nano-PbO to be applied as electrode material in the manufacturing of new lead-acid batteries.

The claims are:

1. A composition for spent lead-acid battery including lead (II) sulphate (PbSO_4), lead (IV) oxide (PbO_2), residual lead (II) oxide (PbO), lead metal (Pb) and $\text{Pb}_3\text{O}_2\text{SO}_4$ and other metals (Cd, Ag, As, Co, Ca, Cr, Cu, Fe, Mn, Ni, Sb, Se, and Te) at low concentrations.
2. A composition as claimed in claim 1, wherein the spent paste has neutral pH
3. A process for synthesising lead organic precursor for producing nano-PbO from spent automobile lead-acid battery paste comprising the steps of
 - (i) Sourcing spent automobile lead-acid batteries from South-West, Nigeria
 - (ii) Battery discharging and dismantling into different components using hand gloves, hammer, saw blade and pliers.
 - (iii) Homogenisation of the paste by screening to 0.35 mm using scientific sieve of mesh size 48 on a mechanical shaker.
 - (iv) Slurring the paste obtained in step (iii) in 70°C water on a magnetic stirrer for 1 hour to eliminate the presence of residual acidity of the paste (pH 7.27).
 - (v) Reaction of the paste in (iii) separately in ratio 1:10 at pH 3.9, for 30 minutes at room temperature (30°C) with 1M citric acid, 2 M trisodium citrate and 2M 30% hydrogen peroxide; 1M ethanoic acid, 2M sodium ethanoate, and 2M 30% hydrogen peroxide; 1M methanoic acid, 2M sodium methanoate and 2M 30% hydrogen peroxide in the ratio 2:1:2 respectively with the mixing sequence of acid, salt and hydrogen peroxide solutions, followed by paste addition or mixing of acid and salt solutions, followed by paste addition and then hydrogen peroxide to select appropriate reagents and mixing order.
 - (vi) Reacting the paste in (iii) with 1M citric acid, 2 M sodium citrate, 2M hydrogen peroxide with mixing order of citric acid and sodium citrate solutions first, followed by paste and then hydrogen peroxide at different concentrations of citric acid (1 -3.0 M), paste to solution ratio (20-200g/L), temperatures ($30\text{-}40^\circ\text{C}$), stirring rate (500-700 rpm), reaction time (30-240 minutes).

(vii) Synthesising lead citrate precursor from the paste as obtained in (iii) at 1M citric acid, 2 M sodium citrate, 2M hydrogen peroxide (2:1:2) at pH 3.9, 100 g/L paste to solution ratio, 30 °C temperature, 500 rpm stirring rate and 3 hours reaction time, dried at 70°C and evaluating the chemical phases, structural and microstructural properties therein

(viii) Calcination of sample as obtained in (vii) in static air at 400 °C for 30 minutes at heating rate of 10 °C min⁻¹ to obtain iron, carbon and sulphur-free nano-PbO useful for production of new automobile lead-acid battery.

4. A process that completely removes iron, carbon and sulphur from the final product
5. A process wherein mixing of citric acid and sodium citrate first, followed by addition of paste, then hydrogen peroxide as the mixing order leading to maximum yield of Pb citrate precursor.
6. A process wherein iron, carbon and sulphur-free nano-PbO powder with particle size of 60-300nm is produced from simultaneous leaching, desulphurisation, reduction and precipitation of the whole content of the pastes including PbSO₄, PbO₂, residual PbO, Pb and Pb₃O₂SO₄.