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Combustion synthesis of PbO from lead carboxylate precursors relevant to developing a new method for recovering components from spent lead–acid batteries

Jiakuan Yang,[a,b]* Ramachandran Vasant Kumar[a] and Deepak P. Singh[a]

Abstract

BACKGROUND: In the conventional recycling process, lead battery pastes are recovered as metallic lead by using an energy intensive decomposition and reduction process. Decomposition of $PbSO_4$ requires the use of relatively high temperature and causes environmental pollution, i.e. emission of SO_2 and lead particulates. A new process for treating the pastes at low temperature has been developed.

RESULTS: Three major lead compounds are individually reacted with an aqueous solution of citric acid in order to leach and to crystallize lead citrate precursors, which are then subjected to calcination at relatively low temperatures to recover the lead directly as PbO the most common active material for preparing pastes for a new battery. Characterization of the citrate precursors have been carried out using DSC, XRD, and SEM. The combustion products were characterized by XRD and SEM.

CONCLUSION: Lead(II) oxides along with a small amount of lead metal are the combustion products, which can be produced at a relatively low temperature of 350 °C. Resulting morphologies show that combustion products are in the 100–200 nm size range, providing high-surface-area PbO for making new battery paste materials. The work is aimed to develop a sustainable process for recovering lead from spent lead battery paste.

Keywords: lead-acid battery; lead carboxylate; combustion synthesis; recycling

INTRODUCTION

Of the nearly 7 million tonnes per year (mtpy) of lead production worldwide, more than 70% is used in batteries. Over half of the total lead is derived from recovering lead from used batteries, and the rest from galena (PbS) based ores. In the near future it is possible to imagine that over 95% of all lead (10 mtpy by 2012) will be used in batteries for vehicles and emergency power supplies and most of this demand will be met by recovering lead from used batteries. Lead–acid batteries represent the highest recovery rate of any commercial product, and recovery rates of 95–97% have been achieved since the late 1990s.

It is a misnomer to categorize this process as recycling. Since lead in used batteries is mainly in the form of lead sulphate ($PbSO_4$) and some unreacted PbO and PbO_2, it is recovered as lead using an energy-intensive decomposition and reduction process. Decomposition of $PbSO_4$ requires relatively high temperature using coal or coke as the source of energy. Thus the smelting route is associated with a large amount of CO_2 emission, together with the criteria pollutants particulate lead and SO_2, and energy usage of 4–10 kW h kg^{-1} lead. Treatment of harmful gaseous emissions is both expensive and legally binding, and environmental legislations continue to get stricter.[1] For each tonne of smelted lead, it is necessary to clean 30 000–40 000 m^3 of process gases, which must be treated by using very expensive equipment.

Several research projects, pilot plants and commercial methods have been developed to overcome these problems, especially with sulfur encountered from the smelting route. A common method is to use NaOH (aq) or Na_2CO_3 (aq) solutions to fix sulfur as soluble Na_2SO_4 (aq) which can be crystallized as a viable by-product. Prengmann developed a method for desulfating lead–acid battery mud by converting lead sulfate ($PbSO_4$) into precipitated lead carbonate ($PbCO_3$) or hydrate.[2] The insoluble $PbCO_3$ or $Pb(OH)_2$ collected as a sludge or filter cake is then routed to the smelter. Unfortunately it has not been possible to completely avoid the retention of some sulfur in the sludge/filter cake and the associated SO_2 acid-gas emission. In order to eliminate smelting altogether, some of the new processes have dissolved the lead sludge/filter-cake in acids such as H_2SiF_6 or HBF_4 to recover lead by electrowinning. This is capitally intensive and is often suitable only

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* Correspondence to: Jiakuan Yang, School of Environmental Science and Engineering, University of Huazhong University of Science and Technology, Wuhan, Hubei, 430074, P.R. China. E-mail: jkyang@mail.hust.edu.cn

a Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK

b School of Environmental Science and Engineering, University of Huazhong University of Science and Technology, Wuhan, Hubei, 430074, P.R. China

for large-scale operations entailing large movement of hazardous raw materials.[3] The process is even more energy intensive than smelting at an overall energy intensity of 10–15 kW h kg^{-1} of lead if the purchased electricity is derived from fossil-fuel-combustion power plants typically at 30–40% efficiency.

Once lead is recovered it is then re-oxidized to PbO granules and made into pastes with H_2SO_4 (aq) to apply to lead grids in the manufacture of battery electrodes.[4] After assembling the battery, electrical energy is used to convert PbO to Pb in the anode and PbO_2 in the cathode.[5]

A lead battery is a very versatile system for use in vehicles for starting, lighting and ignition (SLI). The energy density of a lead battery is 30–50 Wh calculated with one kg of Pb equivalent as the basis. This amount derived from a battery is 2–3 orders of magnitude lower than the energy required to recover the lead from a spent battery using current recovery methods (at 4000–10 000 Wh kg^{-1} lead equivalent). There is no doubt that batteries are convenient sources of energy; but these calculations show that it is not sustainable with respect to the efficient use of energy. It is sometimes erroneously suggested that since a lead battery is recharged and discharged several times, the cumulative energy available should be considered over the full cycle of use. Such arguments fail to consider that each charging part of the cycle is associated with use of energy which is always higher than the energy derived from discharge.

However, as it is not an option not to recover lead from used batteries an alternative process has been developed for treating components of spent lead–acid batteries at a lower temperature to recover PbO for direct used as active material for new batteries. A sustainable process for recovering lead components with lower energy consumption has been proposed and is currently being piloted as an alternative to conventional methods.[6] Combustion synthesis of single or multicomponent metal oxides from metal carboxylate precursors has been investigated by many researchers who have shown the feasibility and huge potential for such a low temperature process that can avoid both the pyrometallurgical and electrowinning routes.[7–10] Preliminary work with the individual components has been reported.[11,12] Further crucial work has been carried out in this work, with a view to providing optimized data for treating real battery wastes.

In general, the chemical compositions of waste lead battery pastes comprise lead sulfate (~60%), lead (IV) dioxide (~28%), lead (II) oxide (~9%), and a small amount of lead metal (~3%). In this paper, the three major components ($PbSO_4$, PbO_2, and PbO) of waste lead acid battery scrap were individually treated by aqueous citric acid solution to generate lead carboxylate precursors. Metallic lead particles leached in a similar fashion to PbO particles except that the maximum temperature rise during leaching is 1 °C higher with Pb than with PbO. Given that the typical PbO/Pb wt ratio in a spent paste is in the range 5 : 1 to 3 : 1, this small effect will be mostly masked. Therefore results for metallic Pb particles are not discussed and assumed to be subsumed within PbO leaching. The combustion products from the three lead carboxylate precursors in this paper were investigated and reported in this paper.

EXPERIMENTAL

Chemicals

Lead(II) oxide powder (PbO, >99.9% purity), lead (IV) dioxide (PbO_2, >97% purity), and lead sulfate ($PbSO_4$, >99% purity) were simulated as the three major components in waste lead–acid battery scrap.

Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, 99.5% purity) was used to prepare the citric acid aqueous solution in distilled water for leaching-crystallization. Hydrogen peroxide (H_2O_2, >30% w/v) was used as a chemical reducing agent during leaching of PbO_2. Trisodium citrate hydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, >99% purity) was used as the desulfating agent during leaching of $PbSO_4$. All chemicals were purchased from Fisher Scientific Company, and used as received.

Synthesis of lead carboxylate precursors

Lead(II) oxide powder was added to citric acid solution at a molar ratio of 1 : 1.5 (Pb : citric acid) and a solid/liquid (S/L) mass ratio of 1 : 3. Lead(IV) dioxide powder was added to citric acid solution and 30% hydrogen peroxide solution, at a molar ratio of 1 : 4:4 (Pb : citric acid : peroxide hydrogen) and a S/L mass ratio of 1 : 5. The hydrogen peroxide served as a reduction agent to convert lead(IV) into lead(II). During reduction, bubbles of oxygen were emitted from the solution. Lead sulfate powder was added to citric acid and trisodium citrate solution at a molar ratio of 1 : 1:2 (lead: citric acid: trisodium citrate), and a S/L mass ratio of 1 : 5. Trisodium citrate contributed the desulfatization by generating soluble sodium sulfate. A sample (5 g) of lead(II) oxide, lead(IV) dioxide, and lead sulfate was used in the leaching process, which was carried out under magnetic stirring (500 rpm) for 1 h at room temperature. After completion of the reaction, the resulting precipitate was allowed to settle for 15 min and then the collected solids were washed with distilled water, filtered and dried at 65 °C to give lead carboxylate precursors. Three different lead carboxylate precursors from PbO, PbO_2, and $PbSO_4$ are identified as precursor I, precursor II, and precursor III, respectively, in the following sections.

After leaching, filtration and washing, the concentration of lead in the residual solution was analyzed by ICP-OES Spectrometer (Liberty series II, Varian Australia).

Characterization of lead carboxylate precursors

Thermal analyses of the precursors were performed in aluminum crucibles by SDT (simultaneous differential scanning calorimetry – thermal gravimetric analysis), using a TA Instruments Q600 SDT with air flow of 100 cm^3 min^{-1} up to 1400 °C at a heating rate of 10 °C min^{-1}. Morphology studies were carried out by scanning electron microscopy (JEOL 820 SEM, Tokyo, Japan) operated at 10 kV with samples coated with gold. X-ray diffraction (XRD) data were collected from powder samples using a PW1820 Goniometer (Philips, PANalytical B.V. Almelo, the Netherlands) with Cu Kα radiation ($\lambda = 1.54056$ Å) at a scanning rate of 0.005° s^{-1} for a range of 2θ from 3° to 80°.

Synthesis of the combustion products from lead carboxylate precursors

The three precursor powders were calcined at 300, 350, 400, and 450 °C for 1 h in static air. Precursor I (PbO) was calcined at 350 °C for 10, 20, 60, 80, and 120 min in static air. The weight loss was checked for each set of experiments.

Characterization of combustion products

The crystalline phases of the decomposed samples were identified by powder X-ray diffraction (Philips, PW1820 Goniometer, PANalytical B.V. Almelo, the Netherlands) under the above conditions over the 2θ range from 10° to 140°. Scanning electron microscopy (SEM) images were investigated with a field-emission microscope (JEOL 6340F FEGSEM) operated at 5 kV after the combustion products samples were coated with platinum.

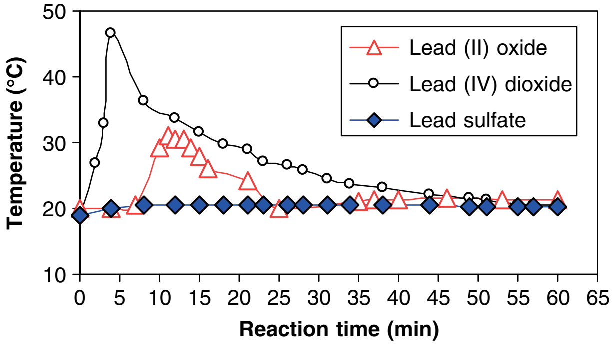

Figure 1. Relationship between temperature change and leaching reaction time.

RESULTS

Leaching-crystallization and the recovery of lead

The relationships between temperature changes and reaction time are shown in Fig. 1 showing that the leaching-crystallization reactions of all the three lead citric acid complexes are exothermic. Leaching of lead(IV) dioxide shows the strongest exothermic effect, with the temperature increasing to a peak temperature of 48 °C. This might be the result of a cooperative effect of hydrogen peroxide reduction and citric acid leaching. Leaching of lead sulfate shows the weakest exothermic effect. In general, the three leaching processes could be completed in 1 h and as stirring rates do not affect the leaching or recovery it suggests that the reactions are under chemical control. However, it is important to maintain the stirring to avoid settling of the solid reagents and products. Begum *et al.*[13] studied the kinetic mechanism of dissolution of lead sulfate with aqueous trithanolamine solution and inferred that the process was partially controlled by the rate of the chemical reaction at room temperature. Ke *et al.*[14] showed the leaching of PbO_2 particles in an alkaline sodium hydroxide solution containing glycerol might be described by a shrinking core model, and the leaching process was controlled by the rate of the chemical reaction.

The mass of solid products from the carboxylate precursors and the concentration of lead left in solution are summarized in Table 1 showing in each case lead recovery >97%.

Crystallization characteristics of the lead carboxylate precursors

The XRD patterns of the three precursors are shown in Fig. 2. Precursors from PbO and PbO_2 leaching agree with lead citrate structural data (Cambridge Structural Database (CSD)). Kourgiantakis *et al.*[15] suggested by analytic calculation that the chemical formula of lead citrate is $[Pb(C_6H_6O_7)]\cdot H_2O$ (MW 415.33). Because the XRD patterns of precursor III do not match the $[Pb(C_6H_6O_7)]\cdot H_2O$ data in CSD or any other known data, the chemical formula of precursor III is best described as $[Pb(C_6H_5O_7)_m]\cdot nH_2O$, where the values of m and n have to be deduced experimentally.[16] None of the starting lead compounds were identified in the XRD patterns (b), (c) and (d), indicating that the leaching was complete.

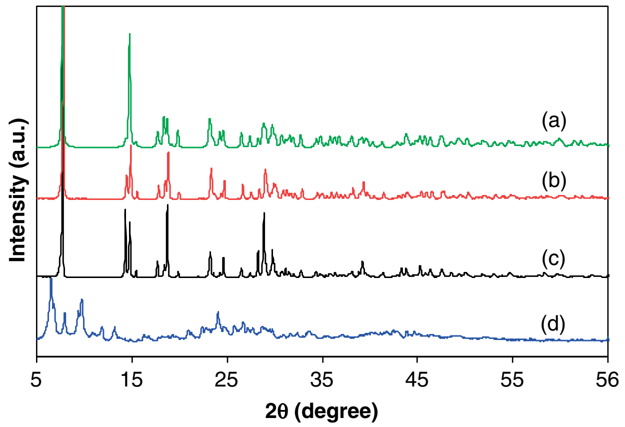

Figure 2. XRD patterns: (a) standard lead citrate in CSD and the precursors from (b) PbO, (c) PbO_2 and (d) $PbSO_4$.

Morphologies of the three precursors (Fig. 3) show that precursors I and II are sheet-shaped crystals with lengths 10–20 μm, widths 2–5 μm and thickness 0.5 μm, but precursor III particles show irregular shapes with a size range 1–10 μm.

Thermal characteristics of the lead carboxylate precursors

The TGA/DSC curves of the precursors are shown in Fig. 4. The curves of precursors I and II nearly overlap and it is concluded these precursors are identical consistent with XRD and SEM results. The first stage of weight loss of the precursors is observed in the range 120–170 °C, identified as a dehydration reaction, accompanied by an endotherm in the DSC curves. During this dehydration the weight loss of precursor III is about 5.5%, which is higher than the weight loss of precursors I and II, at about 4.2%. The second stage of weight loss is in the range 170–350 °C ascribed to decomposition of the carboxylate, accompanied by two exotherms in the DSC curves. The total weight loss for precursor III in this stage is about 38.3%, much lower than that for precursors I and II, at about 49.8%. Stoichiometric calculations indicate that the composition of the product from precursor III can be expressed as $[3Pb\cdot 2(C_6H_5O_7)]\cdot 3H_2O$, compared with lead citrate ($[Pb(C_6H_6O_7)]\cdot H_2O$) for precursors I and II.

At temperatures higher than 350 °C, both the weight loss and heat flow are constant up to 872 °C the melting point of PbO, as shown by the endotherms. Thus it is seen that the decomposition

Table 1. The concentration of lead in the separated solution and the recovery of lead

Original lead compound	Mass of original lead compound (*g*)	Moles of original lead compound	Concentration of lead in the residual solution (mg L^{-1})*	Moles of lead in the residual solution	Percentage recovery of lead
PbO (99.9%)	5.000	2.238E-02	165.11	1.992E-04	99.11
PbO_2 (97%)	5.000	2.028E-02	15.10	1.822E-05	99.91
$PbSO_4$ (99%)	5.000	1.633E-02	290.30	3.503E-04	97.86

* Each solution was diluted to 250 mL.

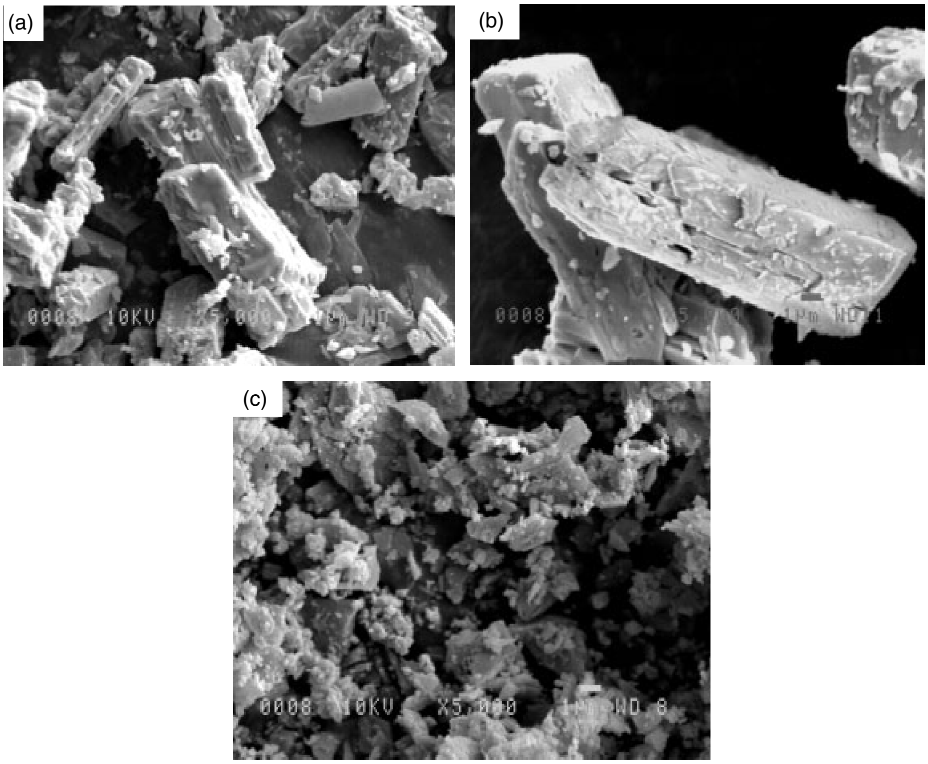

Figure 3. SEM images of precursors from (a) PbO, (b) PbO_2 and (c) $PbSO_4$.

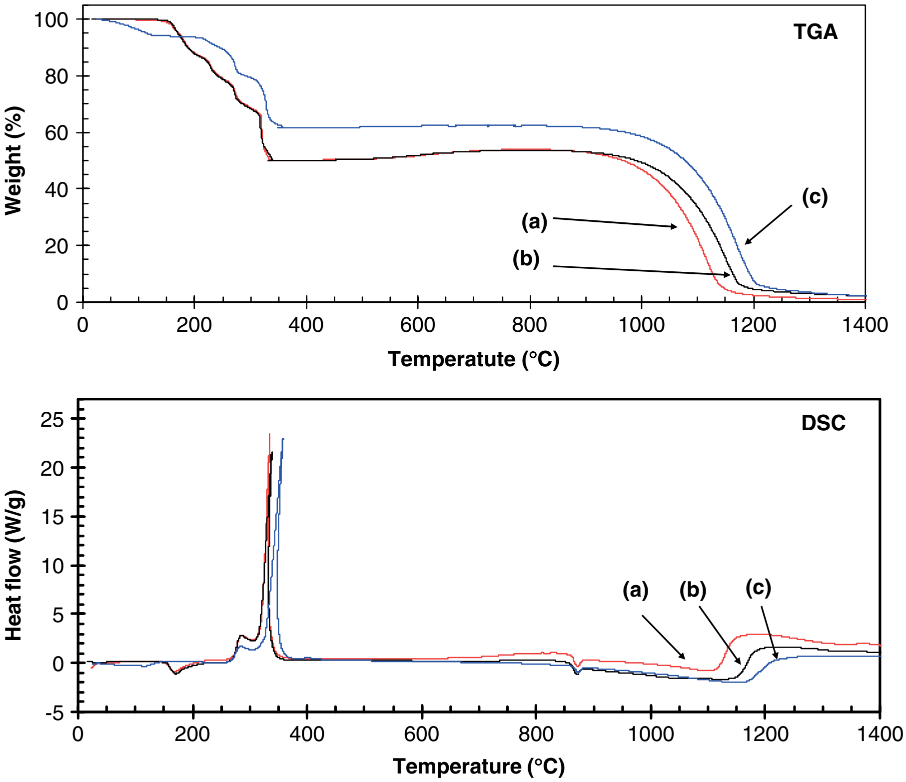

Figure 4. TGA/DSC curves of precursors from (a) PbO, (b) PbO_2 and (c) $PbSO_4$.

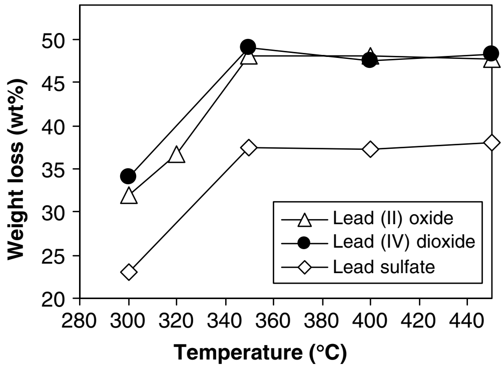

Figure 5. Effect of calcination temperature on percentage weight loss of precursors after heating for 1 h.

of the carboxylates is complete at 350 °C. Therefore, a calcination temperature of the precursors for synthesis of PbO can be chosen about 350 °C.

Calcination

The weight losses of the precursors on heating for 1 h at various calcination temperatures are shown in Fig. 5. For precursor I from PbO, three experimental temperatures, 300, 320 and 350 °C, were selected in the preliminary experiments. The weight loss increased significantly with increasing calcination temperature. Therefore, in subsequent calcination experiments temperatures intervals of 50 °C were deemed sufficient. For all three precursors, the weight loss increased as the calcination temperature increased and then was relatively stable over the range 350–450 °C, indicating complete decomposition at 350 °C. These results (Fig. 5) are fully consistent with the DSC observations in which the major exothermic peaks end at about 350 °C. The weight losses at $\geq$350 °C of both precursors I and II are 48%, significantly more than that of precursor III at 38%. This difference is also consistent with results of weight loss at $\geq$350 °C in the TGA curves (Fig. 4).

A study of the effect of time of heating on weight loss at 350 °C showed that after 20 min there was no change suggesting that for practical applications the reaction is fairly rapid.

The XRD patterns of the combustion products

The XRD patterns of the products of combustion at different temperatures in static air for 1 h from the precursors are shown in Figs. 6(a), (b), and (c). The combustion products are amorphous at 300 °C, and transform into crystalline phases of both massicot (orthorhombic lead oxide) and lead metal at 350, 400 and 450 °C. This indicates that the carboxylates decompose completely above 350 °C, consistent with the results of TGA/DSC (Fig. 4) and weight loss (Fig. 5). The relative intensity of the peak of the lead metal phase decreases as the calcination temperature increases from 350 to 450 °C, while the relative intensity of the peak of the massicot phase increases over the same temperature range for precursors I and II, (Figs. 6(a) and (b)). This indicates that ratio of PbO to Pb increases with temperature. Semi-quantitative results of the percentage of PbO and Pb are calculated by the Rietveld method[17] (Fig. 7). With precursor III, PbO is the predominant phase at all temperatures in the 350–450 °C range, while for samples from the other two precursors, the ratio of PbO to Pb increases with temperature. This results show that it is possible to control the degree of oxidation to achieve different PbO/Pb ratios.

Among three starting materials $PbSO_4$ is the major component in a spent battery which is also relatively the most difficult component to leach and/or to decompose. As X-ray reflections for lead sulfate were not detected in the combustion products from precursor III (Fig. 6(c)), this indicates good desulfation of lead sulfate.

SEM images of the products of combustion synthesis

SEM images of the products of combustion from the precursors at different temperatures in static air for 1 h are shown in Figs. 8, 9 and 10. As shown the products form porous structures, indicating that the carboxylates are not completely decomposed at 300 °C and this porous polymeric structure is consistent with the amorphous phase in the XRD pattern at 300 °C, (Fig. 6). In Figs 8–10(b), at 350 °C the products show particles of 100–200 nm size, however, with a non-uniform distribution pattern. When the calcination temperature is increased to 400 or 450 °C, the particles agglomerate and then grow, as shown in Figs 8–10(c) and (d).

DISCUSSION

According to the XRD results and SDT of the precursors, the chemical formula of precursors I and II is $[Pb(C_6H_6O_7)]\cdot H_2O$, and the chemical formula of precursor III is $[3Pb\cdot 2(C_6H_5O_7)]\cdot 3H_2O$. Therefore, the synthesis of the lead(II) citrate from lead(II) oxide and lead(IV) dioxide follows reactions (1) and (2), respectively. However, the synthesis of precursor III from lead sulfate is accomplished according to the reaction Equation (3). The exact role of citric acid in reaction (3) is not clear, and is currently being investigated.

$$PbO + C_6H_8O_7 \cdot H_2O \xrightarrow{H_2O} [Pb(C_6H_6O_7)] \cdot H_2O + H_2O \tag{1}$$

$$\begin{aligned} &PbO_2 + C_6H_8O_7 \cdot H_2O + H_2O_2 \xrightarrow{H_2O} [Pb(C_6H_6O_7)] \cdot H_2O \\ &\quad + O_2 \uparrow + 2H_2O \end{aligned} \tag{2}$$

$$\begin{aligned} &3PbSO_4 + 2[Na_3C_6H_5O_7 \cdot 2H_2O] \rightarrow [3Pb \cdot 2(C_6H_5O_7)] \cdot 3H_2O \\ &\quad + 3Na_2SO_4 + H_2O \end{aligned} \tag{3}$$

Solids were obtained by filtering the product at the end of reaction and drying. The yields (Table 2) were calculated assuming this solid from PbO and PbO_2, was lead(II) citrate ($[Pb(C_6H_6O_7)]\cdot H_2O$), and the product from $PbSO_4$ was $[Pb(C_6H_5O_7)_n]\cdot H_2O$. The maximum yields for the solid product from PbO and PbO_2 are about 96 and 99%, respectively. Assuming a similar maximum yield of the product from $PbSO_4$ it can be deduced that n should be equal to 0.665, assigning a value of 2/3 consistent with the results of TGA/DSC. Thus the chemical formula of the solid from $PbSO_4$ can be expressed as $[3Pb\cdot 2(C_6H_5O_7)]\cdot 3H_2O$ for which no XRD pattern is available in the literature.

Initially three chemicals, i.e. PbO, PbO_2, and $PbSO_4$, were used as the starting material in the leaching process, but real lead paste from spent lead batteries may contain varying composition and particle sizes of these compounds as well as some metallic lead particles and the compounds can also be present in different crystallographical forms. We carried out leaching work with different particle sizes and structures to find that the final citrates are not dependent upon these variations. Our aim is to investigate whether we can convert such lead based raw materials directly to PbO after leaching and combustion.

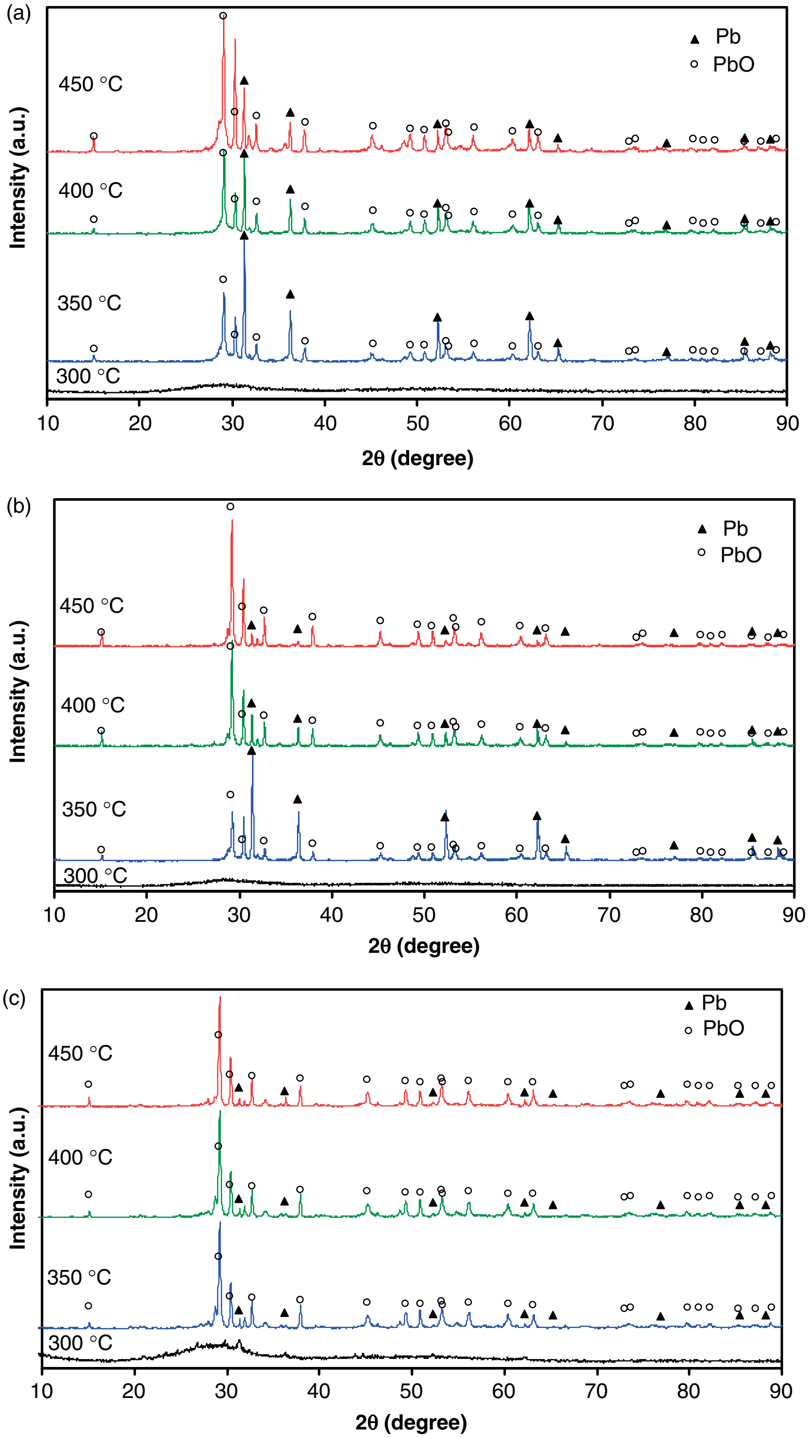

Figure 6. XRD patterns of combustion products from (a) precursor I, (b) precursor II, and (c) precursor III after heating for 1 h.

The thermal decomposition of metal carboxylates in oxidizing atmospheres generally leads to the formation of the metal oxide (or oxides), carbon dioxide and water. In vacuum or in inert atmospheres, however, the solid products may also contain the metal and/or metal carbide. Brown[14] studied the thermal decomposition of lead citrate in inert atmospheres, and the results showed that pyrophoric metallic lead and carbon particles were produced. Lead(II) oxide powder is commonly used as the initial paste in the production of a lead acid battery. Thus it is advantageous to produce PbO powder directly by using air as the oxidant in the combustion of the precursors.

If the thermal decomposition products of the precursors I, II and III are pure lead(II) oxide, the expected weight loss of precursors can be calculated. The calculated results are summarized in Table 3, and compared with the results from SDT and calcination experiments. The results show that the calculated values of weight loss from the chemical formula are consistent with the results of TGA and calcination experiments.

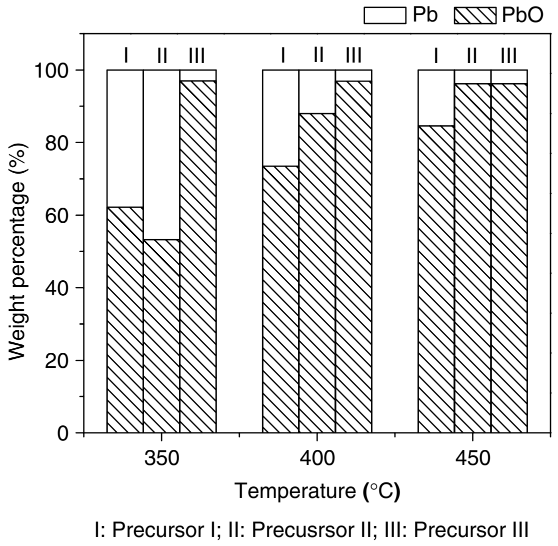

Figure 7. Effect of the calcination temperature on the PbO and Pb percentages in the combustion products after 1 h heating.

Another interesting result is that the ratio of PbO to Pb increases as the calcination temperature increases from 350 to 450 °C (Fig. 7). Further work is being carried out to control the degree of oxidation by controlling the variables in the combustion process such that pure metallic Pb or pure PbO_2 can be produced for direct use as anode and cathode components.

In this novel process, no lead fume is produced in the exhaust gas since the calcination of the precursors is carried out at less than 400 °C, which is much lower than the vaporization temperatures of lead and lead compounds. The exhaust gas comprises CO_2, H_2O, and some residual undecomposed hydrocarbons, which can be treated with a bag house collector system combined with activated carbon adsorption. Generally, a closed recirculation system can be used to circulate citric acid solution in the leaching process.

CONCLUSIONS

(1) Precursors synthesized by reacting PbO and PbO_2 with citric acid solutions are identified as lead citrate hydrates which match well with the Cambridge Structural Database. The precursor from $PbSO_4$ is also a lead citrate hydrate but with a different structure and chemical formula. Precursors from PbO and PbO_2 have sheet-like morphologies with lengths of 10–20 μm, and precursors from $PbSO_4$ are irregular shaped particles with a size of 1–10 μm.

(2) Orthorhombic lead(II) oxide (PbO) is the major combustion product of the citrate precursor from $PbSO_4$ and PbO and Pb are the main products from the precursors derived from PbO and PbO_2, with the ratio of PbO to Pb increasing with increasing combustion temperature.

(3) The thermal decomposition of the precursors is complete after 1 h at 350 °C in static air and the resulting particles are in the 100–200 nm size range that tend to agglomerate and become larger at combustion temperatures greater than 350 °C.

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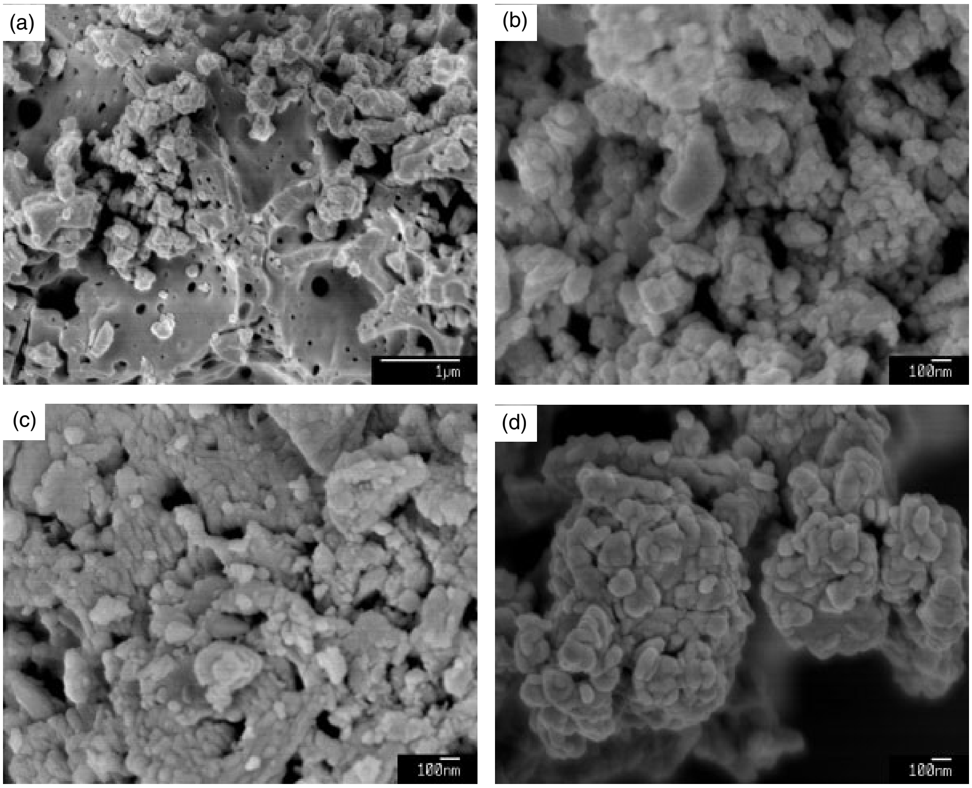

Figure 8. SEM images of the combustion products from precursor I at (a) 300 °C, (b) 350 °C, (c) 400 °C and (d) 450 °C for 1 h.

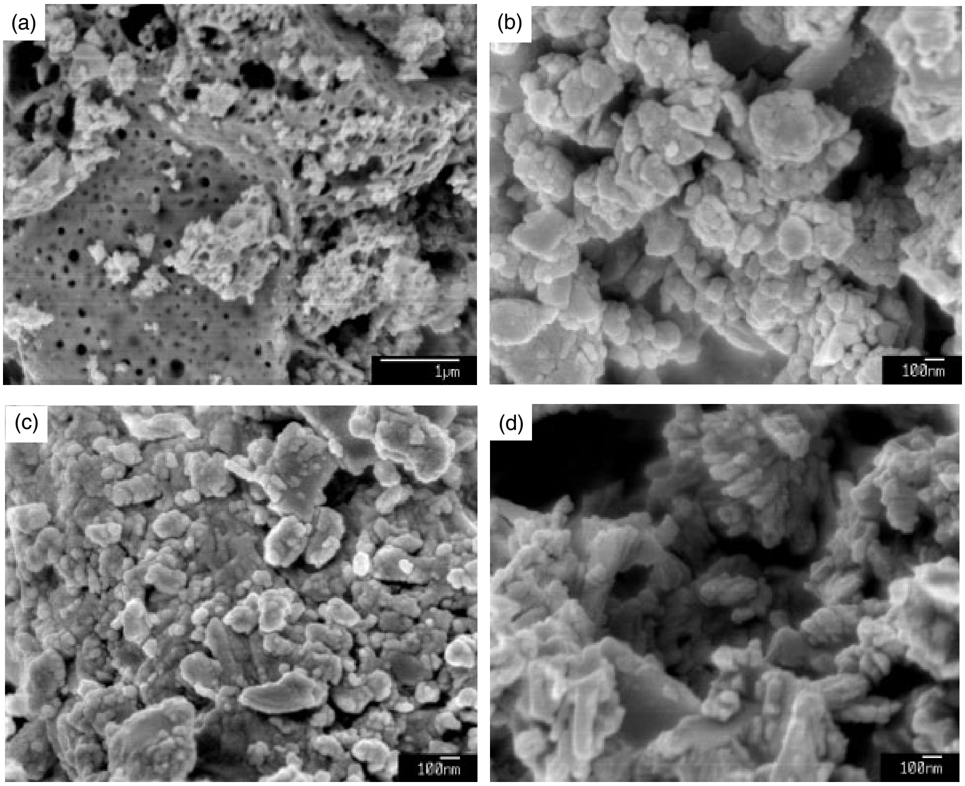

Figure 9. SEM images of the combustion products from precursor II at (a) 300 °C, (b) 350 °C, (c) 400 °C and (d) 450 °C for 1 h.

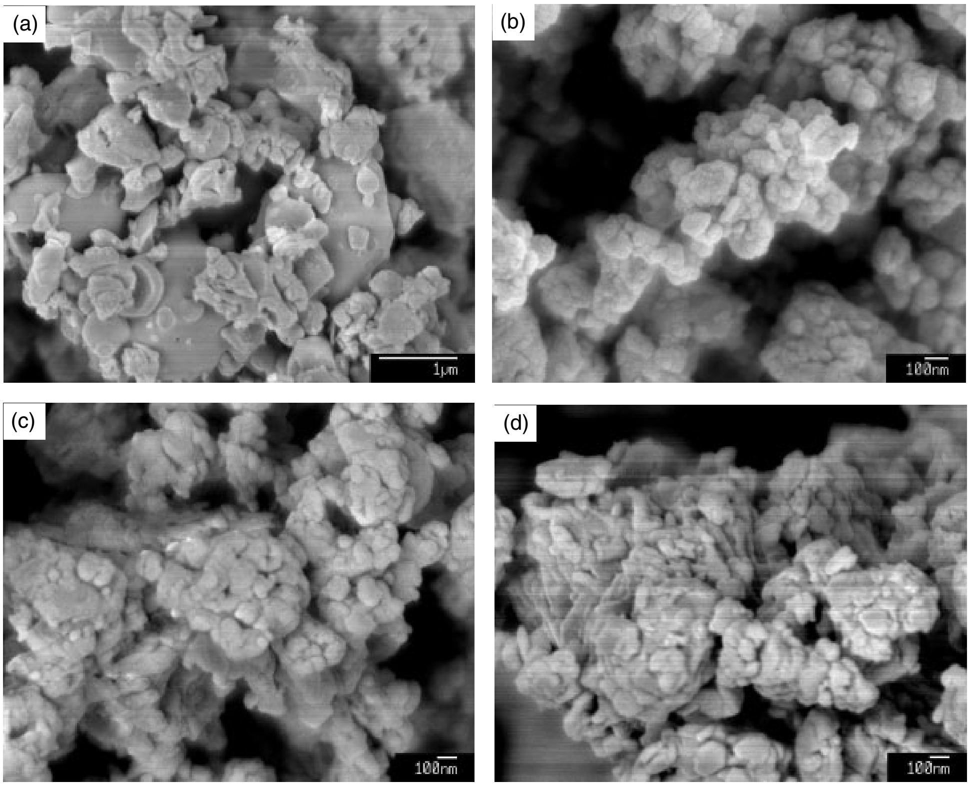

Figure 10. SEM images of combustion products from precursor III at (a) 300 °C, (b) 350 °C, (c) 400 °C and (d) 450 °C for 1 h.

Table 2. The mass of solid products and maximum possible yield

Original lead compound	Moles of original lead compound	Equivalent mass of solid product* (*g*)	Mass of solid product (*g*)	Maximum possible yield (%)
PbO (99.9%)	2.238E-02	9.292	8.960	96.43%
PbO_2 (97%)	2.028E-02	8.420	8.376	99.47%
$PbSO_4$ (99%)	1.633E-02	3.678+3.103n	5.808	5.808/(3.678+3.103n)

* Equivalent mass of solid product calculated according to reaction Equations (1)–(3).

Table 3. Percentage weight loss of the precursors in the combustion process

Precursors	Calc. weight loss of water %	Expt. weight loss after dehydrating (TGA endotherm) %	Calc. weight loss for complete decomposition %	Expt. weight loss after (TGA exotherm) %	Expt. weight loss at calcined temperature 350 °C/1 h %
Precursor I $[Pb(C_6H_6O_7)]\cdot H_2O$	4.3	4.20	46.3	49.8	48.2
Precursor II $[Pb(C_6H_6O_7)]\cdot H_2O$	4.3	4.20	46.3	49.8	49.0
Precursor III $[Pb_3(C_6H_6O_7)_2]\cdot 3H_2O$	5.1	5.50	36.6	38.3	37.5

* Equivalent mass of solid product calculated according to reaction Equations (1)–(3).

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