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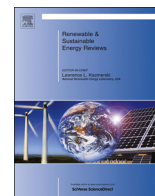
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A critical review on secondary lead recycling technology and its prospect



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ABSTRACT

This article reviews recent studies on the recycling of spent lead paste and describes novel technologies. Although the pyrometallurgical process has been dominant in the secondary lead recycling processes, there has been growing pressure to achieve sustainable greener recycling methods to address the environmental pollution issues caused by emissions of lead particulates and sulfur oxides in the traditional smelting route. The electrowinning process has been studied for many years, but high energy-consumption and emissions of toxic components such as fluoride compounds have caused concerns and hindered rapid growth in industrial application. In last 10 years, many sustainable and environmental friendly processes, such as paste-to-paste recycling and hydrogen-lead oxide fuel cell method have been proposed for recycling spent lead paste from discarded lead acid batteries. Ultrafine lead oxide could be prepared from spent lead pastes via newly developed novel hydrometallurgical routes, and then applied as active materials in the cathode and the anode for making high-performance lead acid batteries. It is a green alternative for recycling of spent lead acid battery and other secondary lead.

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1. Introduction

Lead is a versatile and strategically important metal resource for the industrial development and global economy as it is intrinsically associated with automotive, back-up power and energy storage for renewables [1]. Due to its toxicity, industry related with lead production, recycling, application and consumption must deal with public health and environmental concerns from lead emissions, especially in lead smelting, lead-acid battery production and recycling [2].

The secondary lead produced by recycling process has gradually become the major source of lead in many areas of the world, which will continue to dominate the global lead market [3]. The secondary lead output in developed countries vastly exceed that of primary lead and globally recycled lead accounts for just over 2/3rd of the world output of refined lead [4]. Generally, discarded lead acid batteries (LABs) are the main resource of secondary lead, more than 85% in the total amount of secondary lead [5]. As disposing spent lead is not an option, recycling of spent lead-acid batteries has already proved its value [6]. Nowadays, most of the secondary lead recovery plants are based on pyrometallurgical methods [4]. The emission of sulfur oxides, nitrogen oxides and lead-containing particulate matters from the pyrometallurgical route constitute a serious consequence for the local environment and human lives. Furthermore, major lead poisoning incidents and high lead contamination near the lead factory have already been of great concern to the public. Several electrowinning technique [34–63] have been investigated for the clean treatment of spent battery. Any low temperature process is considered important way forward for eliminating excessive PM_{2.5} (fine particulates less than 2.5 μm measured as aerodynamic diameter) particulates and sulfur dioxide and trioxide. Several studies have reviewed the recycling of lead-acid battery paste using electrowinning techniques, offering favorable comparison with the traditional pyrometallurgy method with respect to direct emissions [7]. However, the electrochemical route is highly energy-intensive and in the medium to long run may not be economically viable for commercial application on account of costs and also from the indirect emissions

associated with purchased electricity if the source is based upon fossil fuels.

Recently, several novel methods for treating of the spent battery have been explored with most of these aiming to offer environmental benefits, lower energy consumption and improved reaction efficiencies. The concept of direct conversion of spent lead battery into a new high-performance battery with minimum number of steps is also worth reporting as such methods have been also considered.

This review introduces the quantity and importance of secondary lead, compared with the primary lead resources. The issues of pyrometallurgy and electrowinning methods for secondary lead recycle are critically analyzed, followed by the summary of the latest progress of novel methods developed in recent years.

2. Lead resources

2.1. Trends in lead production and consumption

In general, there are mainly two basic types of lead resources: primary lead resources and the secondary lead [8]. The quantity of the known lead ore is nearly 85 million tons. Most of the primary lead resources are in the form of minerals, such as, galena (PbS), cerussite (PbCO₃) and sulfuric acid galena (PbSO₄) [8]. Whereas, the secondary lead is mainly produced through the recycling of spent lead-acid batteries [3].

The global lead consumption from 1902 to 2012 is shown in Fig. 1 [9]. The global lead consumption in 2012 has already increased up to more than 10 million tons, nearly twice of the amount only a decade ago.

As shown in Fig. 2 [9], for the post 2000–2001 period, the global secondary lead production is increasing by a large margin, compared to the amount of primary lead production. However, the amount of primary lead production was almost constant from 1970 to 2012, indicating that the industrial demand for primary lead is relatively more stable than that of secondary lead worldwide.

It is important to notice that the secondary lead production in developed countries has exceeded the amount of primary lead

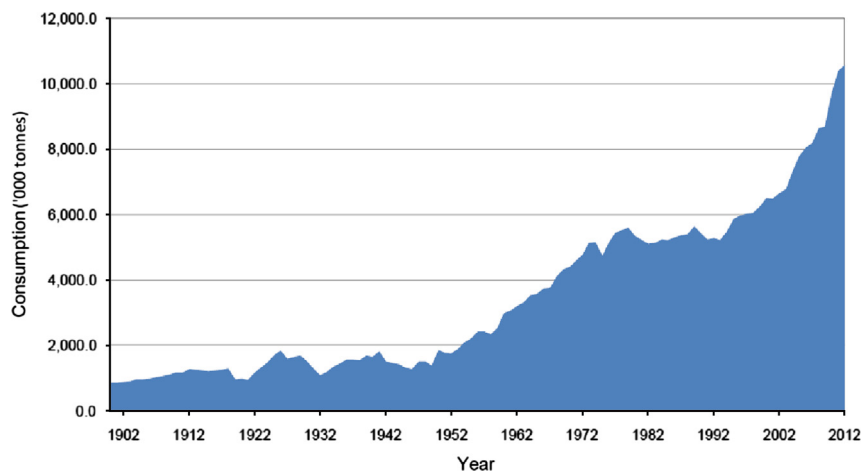


Fig. 1. The global lead consumption from 1902 to 2012 [9].

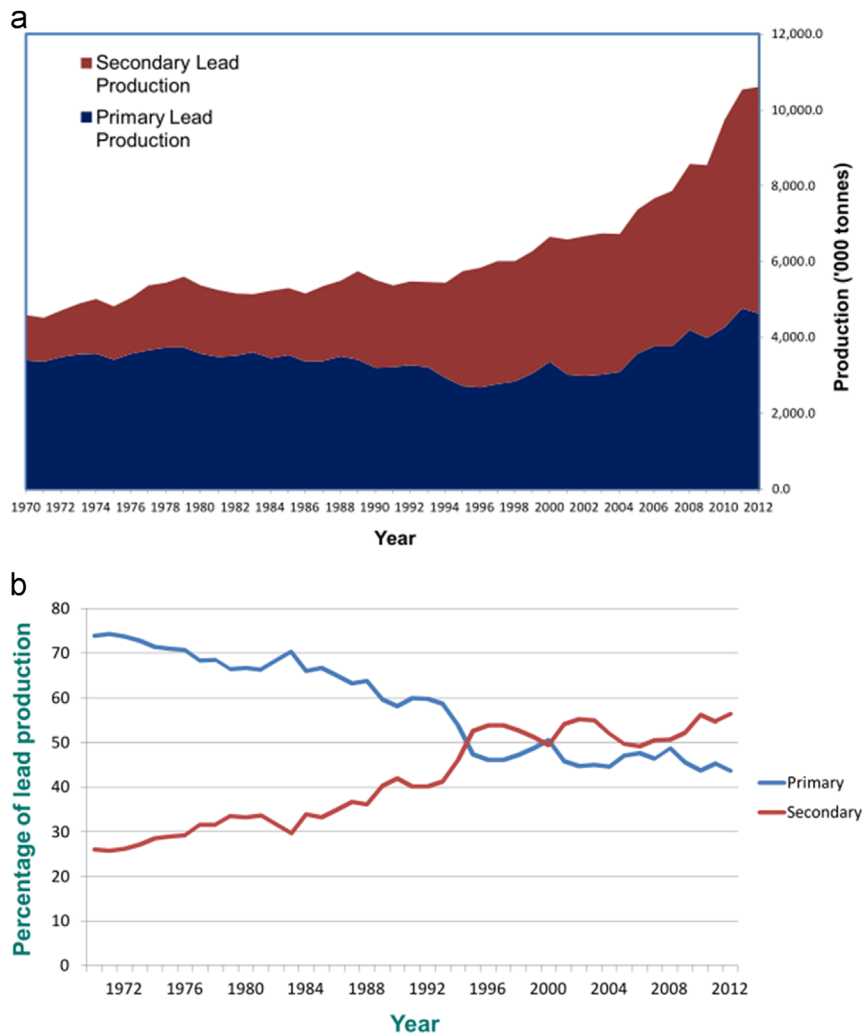


Fig. 2. The amount and percentage of secondary lead and primary lead production from 1970 to 2012 [9].

production. For instance, secondary lead production accounts for more than 80% of total lead production in the United States, 90% in Europe, and more than 95% in some other countries lacking any lead resource; while the global average level of secondary lead has reached 60–66% of the total lead. The official data on secondary lead may be under-reported in emerging markets but also in developed economies to some extent due to the presence of a significant informal recycling sector. Until 2012, the overall official secondary lead production in China was only 29.3%, much lower than the world average, although it is beginning to increase rapidly now [4].

2.2. Secondary lead

Secondary lead mainly refers to the lead recovered from discarded lead acid battery, lead dust, lead pipe, lead glass of liquid crystal display (LCD), and slag from lead smelting process. Among the secondary lead resources, the spent lead acid battery was listed as relatively easier for collection and transportation. Generally estimated, spent/discarded lead acid batteries are the dominant resource of secondary lead, approximately accounting for more than 85% of the total amount of secondary lead [5]. Thus, this article mainly reviews the various spent lead acid battery recycling methods used globally.

The reason for the enormous increase of secondary lead production relates to the continuously growing number of automobile vehicles and electric bicycles, which is much more evident in developing countries, especially in China, which by 2013 has accounted for 40% of the world total lead [10,11]. As listed in Fig. 3, the E-bike sales have already been a favorable choice for urban and rural commuters for its convenience and low price compared to cars. It is estimated that the worldwide lead-acid batteries shipment would increase more or less continuously by a significant margin by 2017 as shown in Fig. 4 despite short term recessionary factors. This suggests that the increasing output of lead-acid batteries would accelerate the lead consumption worldwide. As shown in Fig. 5, a sharp increase of lead consumption for batteries production was observed from 1960 to 2012. This indicates great economic opportunity as well as challenges for efficient and low-cost secondary lead recycling technology.

Furthermore, the amount of secondary lead used for the lead-acid batteries manufacture increased from 0.5 million tons in 2000 to over 3 million tons in 2010 and will account for over 8 million tons in the next several years [12]. The increasing amount of lead-acid batteries would result in more spent lead-acid batteries' accumulation. In order to eliminate the potential environmental pollution caused by secondary lead, more efforts should be made to improve the existing lead recycling infrastructure and to solve the technical challenges for the replacement of traditional smelting method [13–16].

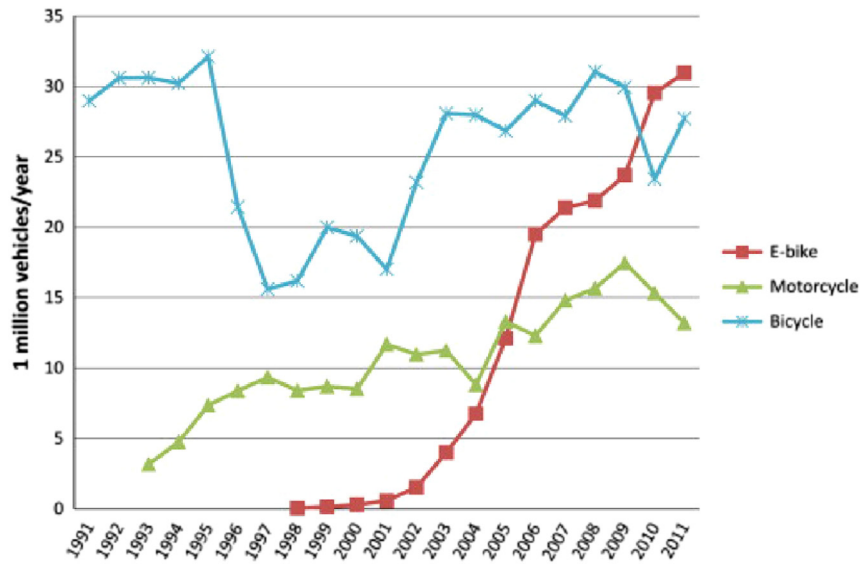


Fig. 3. The amount of E-bike sales and other types of bicycle in China [10].

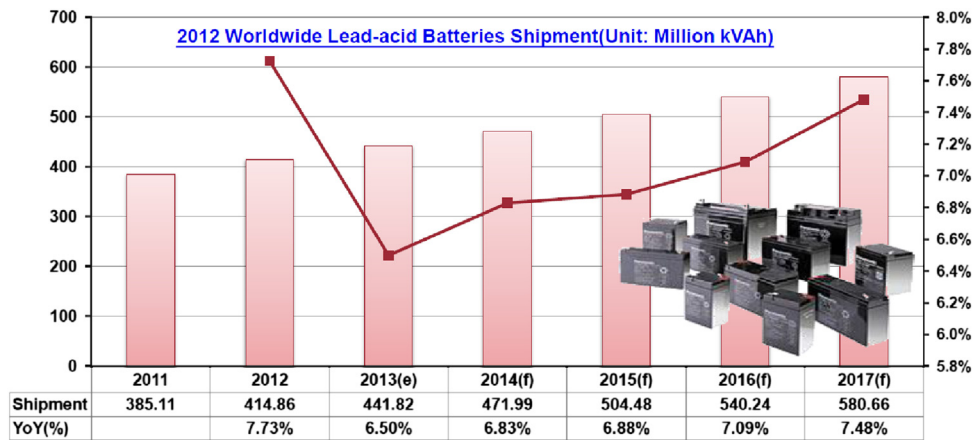


Fig. 4. The worldwide lead-acid batteries shipment and its forecast [12].

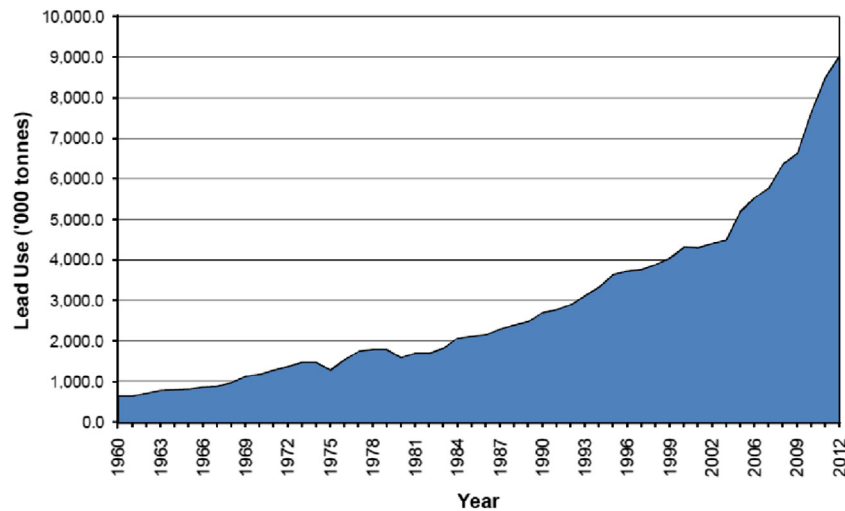


Fig. 5. The lead consumption for batteries between 1960 and 2012 [9].

Overall, the secondary lead has already become the major source of global lead supply, which constitutes a significant percentage of the lead market. Due to the rapid increase of lead acid

batteries production and consumption, the scale of secondary lead recycling would continue to increase dramatically in coming years. Such facts raise the importance of research and development on

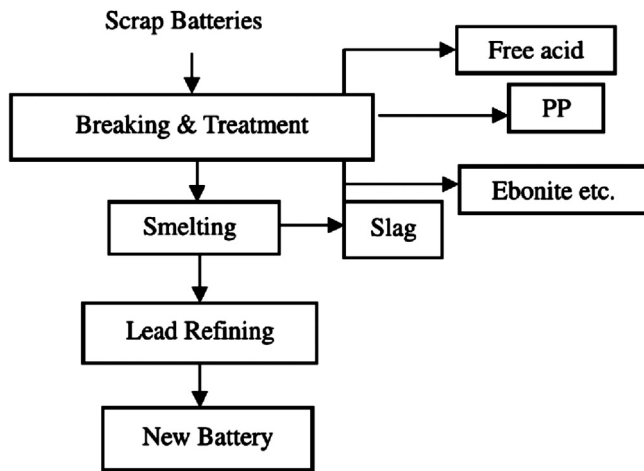


Fig. 6. Flow sheet for recycling of spent battery by unorganized sector [1].

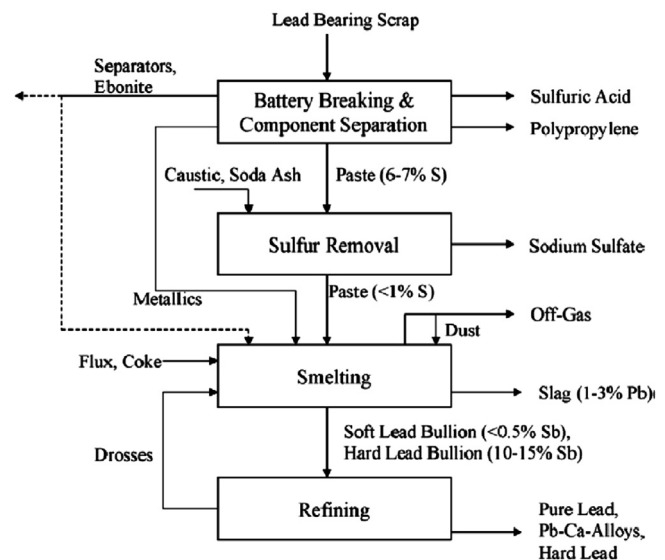


Fig. 7. A typical flow diagram of secondary lead recycling of (ii) [3].

secondary lead recycling from spent lead acid battery, not only in terms of environmental protection but also from the perspectives of resource conservation and economic growth.

3. Progress of secondary lead recovery and recycling

3.1. Traditional recycling route

Currently, the most commonly used method for spent lead acid battery recycling is associated with the crushing process followed by pyrometallurgy route [4]. At the same time, the development of novel furnaces and pretreatment equipment in the pyrometallurgy procedure have been made in recent years. However, the basic flow of lead-acid battery recycling based on smelting method has not significantly changed for a long period of time [17].

3.1.1. Separation and pretreatment process for spent LABs

Prior to recycling, the scrap batteries are firstly crushed in a hammer mill as shown in Fig. 6 [18], where the lead metal, polypropylene, lead grids and slags are effectively separated from the spent lead paste. Among these separated components, the lead grids from the spent battery can be treated at lower temperature to recover the lead metal, given the relatively low melting temperatures of lead and its alloys [1].

3.1.2. Pyrometallurgy

The pyrometallurgical process of spent lead paste requires high temperatures for decomposing the lead sulfate which is the dominant constituent in a spent lead acid battery. The spent lead paste is composed of nearly 60 wt% lead sulfate (~ 60 wt%), but also lead dioxide (~ 28 wt%), lead oxide (~ 9 wt%), and a small amount of metallic lead (~ 3 wt%) [14,19].

The traditional recovery of pastes refining includes the following two route types.

- i. Direct smelting, namely the lead paste was directly treated in smelting furnace at a temperature higher than 1000 °C for decomposing and melting lead compounds with or without desulfurization within the furnace.
- ii. Desulfurization at lower temperatures followed by smelting. The spent paste is treated with a desulfurizing agent such as Na_2CO_3 or NaOH in aqueous solutions near ambient temperatures [20]. The desulfurization process of lead paste takes place at a higher reaction speed when using NaOH solution compared with that of Na_2CO_3 [20]. A typical flow diagram of secondary

lead recycling of (ii) is shown in Fig. 7 [3]. A common factor is the use of $\text{NaOH}(\text{aq})$ or $\text{Na}_2\text{CO}_3(\text{aq})$ solutions to fix S as soluble $\text{Na}_2\text{SO}_4(\text{aq})$ which can be crystallized out as a saleable by-product. The insoluble PbCO_3 or $\text{Pb}(\text{OH})_2$ collected as sludge or filter cake is then routed to the smelter. Unfortunately it has not been possible to fully avoid the retention of some S in the sludge/filter cake and the associated SO_2 emission. The technology of pre-desulfurization process combined with post-paste smelting furnace has seldom been applied in lead recycling companies in China [21].

Based on the difference between furnace and types of smelters employed, the smelting treatment technology can be designed as the QSL process [21,22], Isasmelt Paste Smelting process [23], Kivcet method [21], Kaldo smelting process [21], Rotary or Reverberatory furnace smelting. Blast furnace and Electric-arc based processes can be considered to be less dominant these days with some exceptions.

When lead compounds (sulfates, carbonates, hydroxides or oxides) are reduced to metallic lead at high temperatures, any sulfur is often fixed using slags with Fe or soda in the furnace by forming FeS-PbS dust or a slag containing Na_2SO_4 . Dusts and slags can become hazardous from the lead content that can dissolve in aqueous systems and disposal of hazardous dust or leachable slag is also expensive and harmful to the environment.

Smelting of lead from both the primary and the secondary sources poses potential environmental concerns and requires protection technologies [24]. Mining sector producing raw materials for the pyrometallurgical process is itself responsible for considerable heavy metals release into the atmosphere [25]. The smelting route used for both primary and secondary lead is associated with high lead exposures and toxic air pollution from heavy metals and acidic gases [26,27].

Despite the fact that the paste smelting process has made important progress in energy efficiency, the issue of dust measured as $\text{PM}_{2.5}$, containing lead particulates constitute a major lead poisoning threat to humans, animals, birds, soil and drinking water [28]. Lead emission is particularly harmful in the vicinity of the plant. A study shows that the lead intakes were 6.2 and 50.1 $\mu\text{g}/\text{kg}/\text{d}$ respectively for the adults and children near certain lead recycling plants in China, much higher than the PTWI (Provisional Tolerable Weekly Intake) values [28]. What's worse, the children were the most susceptible to the lead pollution during the

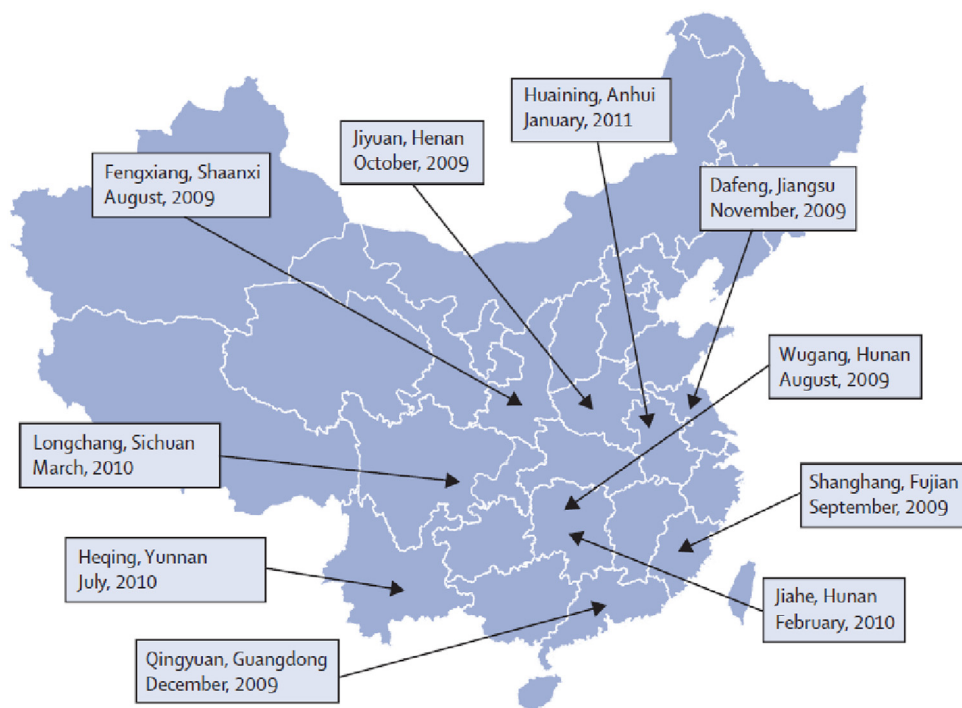


Fig. 8. The major lead poisoning incidents that have occurred in China since 2009 [31].

brain developing period [29,30], which would cause irreversible damage to their critical organs [30,31]. Even lead exposure of low-level is considered to have irreversible effects on brain function [32]. Nearly 4000 children have been reported to be affected by the lead pollution incidents in some certain provinces of China [33]. The release of lead particulates and SO₂ gas into the environment has drawn attention of the local governments, as a result, rules and legal requirements calling for clean production standards were amended and improved [34]. As per the new regulations, all small and medium scale plants without a production certificate would be banned. The lead recycle and lead acid battery manufacture enterprises would not be able to start operation until they clear the environmental inspection from 2015 to 2016 onwards [34–36]. The amount of lead particulates emissions and also SO₂ would be required to be reduced through these strict standards in combination with systematic closure of outdated lead recycling infrastructure. Unfortunately, the long process route from the spent lead acid batteries to new batteries exposes the workers in lead contaminated environment for prolonged periods [37], even if the battery enterprises meet the standard. The major lead poisoning incidents that have occurred in China since 2009 is shown in Fig. 8. Therefore, it is seen as vital to develop and adopt green technologies, systematically replacing old pyrometallurgy routes, for recycling of secondary lead from spent lead acid batteries especially when new investment opportunity arise.

3.2. Electrowinning

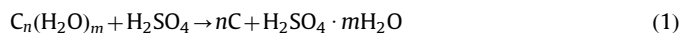
Considering the environmental problems caused by the refining of spent paste in the pyrometallurgy route, electrohydrometallurgical technique, considered as an eco-friendly alternative to pyrometallurgical route, has been developed and used in growing cases for lead recovery from the spent lead-acid battery for the last 30 years [38,39]. In order to evade smelting altogether, some of the new processes have dissolved the lead sludge/filter-cake in powerful acids such as HCl, H₂SiF₆ or HBF₄ in order to help recover lead by electrowinning. Such processes are relatively capital intensive and is often suitable only for large scale

operations entailing large movement of hazardous raw materials from dispersed source to a central facility a feature that is shared with large pyrometallurgical plants. It is also energy intensive at 2–12 kW h per Kg of lead and also polluting, if the purchased electricity for such a process is derived from fossil fuel power plants. The cathodically produced lead is chemically pure but requires re-melting and casting to form lead pigs which are then used for making PbO precursors for new batteries.

3.2.1. Typical electrowinning techniques for spent LABs recycling

In previous electrowinning studies [40,41], the spent lead paste after desulphurization procedure was leached with acid solution from the spent electrolyte, while the lead-pregnant electrolyte was treated with electrowinning route in order to collect the lead from the supernatant which was rich of lead. In this route, the PbO₂ was reduced by the SO₂, which was produced in sulfate decomposition of liquid in the separation procedure.

Marco Olper explored electrowinning route for lead recovery from the spent lead acid batteries [42–45]. The Na₂CO₃ and NaOH were used as the desulphurization reagents. The lead containing products after desulphurization procedure mainly includes Pb, PbO, PbCO₃, PbO₂ and Pb(OH)₂ materials. The desulfurized paste was leached with fluoboric acid, while the remaining undissolved parts of PbO₂ and organic substances with a formula of C_n(H₂O)_m were treated with concentrated H₂SO₄. The reaction of the processes were defined as (1) and (2).



The Pb²⁺ containing solution was prepared for the electrowinning procedure, while the recovered lead cathode was eventually made for electrolytic lead ingots.

The RSR process was developed by Prengaman, which contained a desulphurization treatment using ammonium carbonate reagents for spent lead acid battery paste and a subsequent electrowinning process for lead recovery [7,46–49]. The

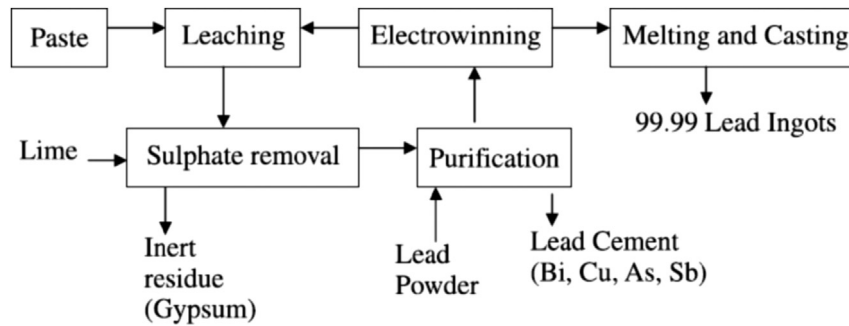
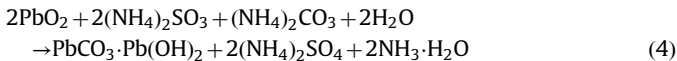


Fig. 9. Flow sheet of the PLACID process.

desulphurization reaction was as follows.



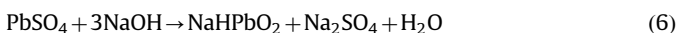
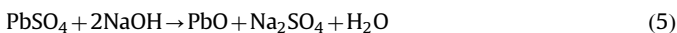
As followed, the PbO_2 may be reduced with the addition of SO_2 to the alkali carbonates such as ammonium carbonate. The reaction products of alkali sulfate or bisulfate would reduce the PbO_2 . The reduction reactions involving in this process were as follows.



These lead compounds were dissolved by suitable acid for electrolytic cell, and generally the fluoboric or fluosilicic acid was preferred. Although the RSR process eliminates the emission of sulfur dioxide and lead dust, the high-energy consumption of electrowinning cell and the direct contact between fluosilicic acid and lead workers were still urged to be solved.

In this route, ammonium carbonate was used for the conversion of lead sulfate, while the lead powder acted as the reducing agent for the conversion of PbO_2 to PbSiF_6 in solution of H_2SiF_6 . The addition of phosphorus was found to have a significant effect on preventing the deposition of lead dioxide on the anode [50–53]. The optimal experimental condition of the electrolysis route was measured as, 180 A/m^2 of current density and 24 h of conducting time at ambient temperature. Nearly 69 wt% of the lead in the electrolyte was deposited at the cathode. The lower recovery ratio of lead should not be overlooked. Furthermore, the addition of lead powder during the reduction of PbO_2 would increase the cost of this process.

Based on the previous research of electrowinning technology, recovery of Pb in alkaline solutions was proposed [48,54,55]. The desulphurization of lead paste occurred by two steps as Eqs. (5) and (6), respectively. The electrolyte was prepared by leaching the desulphurization products of PbO with $\text{NaOH-KNaC}_4\text{H}_4\text{O}_6$ solution. The electrode layer coating was sponge-like and fine-grained. The NaOH was gradually applied in the desulphurization procedure for removal of sulfur [38], then the products were leached by tetrafluoroboric acid through electrowinning technique.

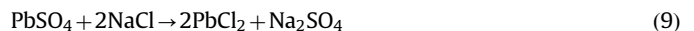


Electrowinning technology in basic media-NaOH-glycerol was proposed by Morachevskii [56], the current efficiency of which would reach up to 85–90%, and the deposit purity of lead could achieve the point of 99.98%. Furthermore, the desulphurization procedure was not required in this route. For considering the shortage of this method, high energy consumption measured to be 400–500 kW h per ton lead output should be considered.

The Electrokinetic (EK) technique [57] is applied to the separation of lead and sulfate from the spent lead paste, while the titanium electrodes (Ti-EK cell) and titanium substrate insoluble

anode electrodes (TISA-EK cell) were compared for improving separation of sulfate and lead. The result shows the superiority of Ti anode over TSIA anode.

In the PLACID process [58,59], lead chloride was formed through the reaction of lead sulfate with chloride, which is different from leaching in acid of HBF_4 or H_2SiF_6 . The chemical reactions of spent paste with the chloride are listed in Eqs. (7)–(9). The lead chloride was then recovered through electrowinning procedure as shown in Fig. 9. The average purity of lead obtained from the PLACID process was measured as 99.995 wt%, and the recovery ratio of Pb was more than 99.5 wt%. However, the energy consumption was nearly 1300 kW h per ton lead output [23].



Lu et al. have developed a solid-phase electrolysis for recovering lead [60–63]. The lead sludge was firstly pasted at the stainless steel cathode. NaOH solution was used as the electrolyte in the phase electrolysis procedure. The electrolysis was performed at a suitable potential ranging from 1.4 to 2.2 V. Lead recovery takes place according to the following reactions (10)–(13). Zhang et al. [64,65] also presented a process consisting of desulphurization, sodium hydroxide leaching, followed by electrowinning procedure. The lead after electrodeposition was treated through oxidation by grinding. The recovery ratio of lead could reach 98%, and the energy consumption was less than 600 kW h per ton lead output.

Cathode:



Anode:



The carbonation leaching of spent lead-acid battery paste was proposed by Lu et al. [66]. This process mainly consists of five steps: (a) carbonation leaching, (b) dissolution, (c) precipitation, (d) synthesis, and (e) desiccation. The final product was lead stearate, which is a relatively crucial material. The leaching recovery of lead could reach 95 wt% at the condition of NTP (normal temperature and pressure). In those days, this method was still a valuable attempt which threw light upon recycle of spent lead paste with hydrometallurgical route based on reagents leaching.

Chen et al. developed the leaching system of HCl-NaCl-CaCl_2 for the treatment of lead skim, followed by conversion in the concentrated NaOH solution at a temperature of about 110 °C. The

recovery ratio of lead reached 92.94 wt% [67]. This complicated and low yield (~92 wt%) process may not be suitable for commercial application of recycling.

Those above mentioned electrowinning process could provide more choices for the lead recovery. However, it is estimated that there are not many lead recycling plant operating on electrowinning process amounting to any significant production capacity.

3.2.2. The challenges in developing electrowinning techniques for spent LABs recycling

- (1) Compared with the pyrometallurgical method, the electrowinning technique was less economically favorable with higher operating costs but also significant capital costs [3]. The higher electricity consumption of this method would increase the expense of its application, which has not been widely adopted by the industrial plant, despite growing interest and new investments in this area [68]. As calculated, the energy cost per metric ton PbO output of electrowinning route was about 78–112 US\$, while the pyrometallurgical method was about 47.3–63.8 US\$ [68].
- (2) The toxic materials were employed in those processes for example the adoption of hexafluorosilicic acid electrolyte. Additionally, the contact between the fluosilicic acid and lead workers still caused health risks.
- (3) The severe corrosion of metallic components in the electrowinning method would increase the expense for the equipment replacement. The acid electrolyte reaction with the metallic components would lead to the dissolution of metal parts of the electrolyte equipment.

3.3. Advances in recycling routes

Although pyrometallurgy is still the predominant methodology for the recycling of spent lead-acid batteries in the recycling enterprises [3], several innovative methods have emerged in the area of lead recovery aiming at better environmental protection and lower energy consumption in the recent 10 years.

In general, those novel lead recycling technologies could be categorized as: (1) reagents leaching followed with cementation reaction; (2) leaching reagents treatment followed by calcination procedure; (3) desulphurization or leaching with novel leaching reagents followed by electrowinning treatment.

3.3.1. Reagents leaching followed by cementation reaction

This method is accomplished in a two-stage process, namely, lead sludge solubilization in urea acetate solution and lead cementation procedures. In this method, the urea acetate solution was prepared by dissolving urea in H₂O/HAc solution, while three types of metallic iron substrates were used as reducing reagents as shown in Fig. 10 [69]. The metallic iron was directly added into the

reactor, and the concentration of lead in solution samples was measured to determine the recovery ratio of metallic lead. The reaction rate was proven to be dependent on the specific surface area of the metallic iron substrates. The recovery ratio of lead would reach 99.7 wt% when using the iron powder as reducing reagents. After cementation procedure, the filtrate solution was added with sulfuric acid to improve the recovery ratio of the low soluble iron sulfate species, which would also achieve the recycling of the urea acetate solution.

The cementation reaction method for the recovery of metallic lead offers two main advantages: (a) it eliminates the emission of sulfur oxides, nitrogen oxides and lead containing particulate matter in the pyrometallurgical route; (b) lower energy consumption than the traditional electrowinning method. However, the percentage of iron in the lead metal was not discussed. Obviously, the iron impurity would decrease the grade of the obtained lead metal and a solution has to be sought.

3.3.2. Desulphurization or leaching followed by electrowinning treatment

Methanesulfonic acid (MSA) was applied for the recovery of cerussite concentrate which is followed by electrowinning of MSA based electrolyte. Flowsheet of this method is shown in Fig. 11. The lead extraction procedure could be termed as 'Leaching-Desulfurization-Relaching'. The lead extraction procedure mainly contains steps of: (a) cerussite concentrate was firstly leached and filtered; (b) sodium carbonate was added for the desulphurization of the residue part consisting of mainly PbSO₄; (c) the residue part was treated using MSA leaching for complete lead extraction. The experimental results show that 98 wt% lead could be recovered in the desulphurization and MSA leaching step. During the electrowinning procedure, calcium ligninsulfonate with concentration of 2.5 g/L would have a significant effect on the morphology of lead after deposit. The cathodic current efficiency of 99 wt% could be achieved, and the specific energy consumption was around 0.53 kWh/kg [70]. Although the objective of this method was cerussite, the similarity of the major component (PbSO₄) in spent lead paste and cerussite was reference for the spent battery recycle. Considering the high overall cost and the lower lead recovery ratio, this multi-step procedure may be not suitable for the industrial application.

A new green hydrometallurgical procedure to recover pure lead based on a hydrogen-lead oxide fuel cell was demonstrated by Pan et al, which would considerably reduce the lead exposure to the environment [68,71–73]. A H₂-PbO fuel cell unit was built, where H₂ was fed into the anode as shown in Fig. 12. The water and electrons were produced in the reaction of H₂ with OH⁻, while electrons were transferred to the cathode. The reactions in the anode and cathode were given as (14)–(16).

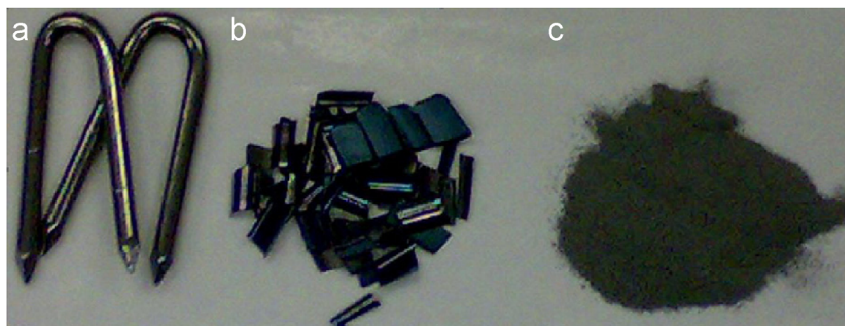
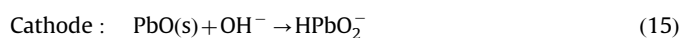
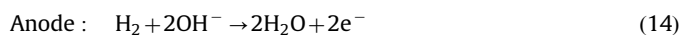


Fig. 10. The reducing agents substrates: (a) nails, (b) shavings, (c) powder. [69].

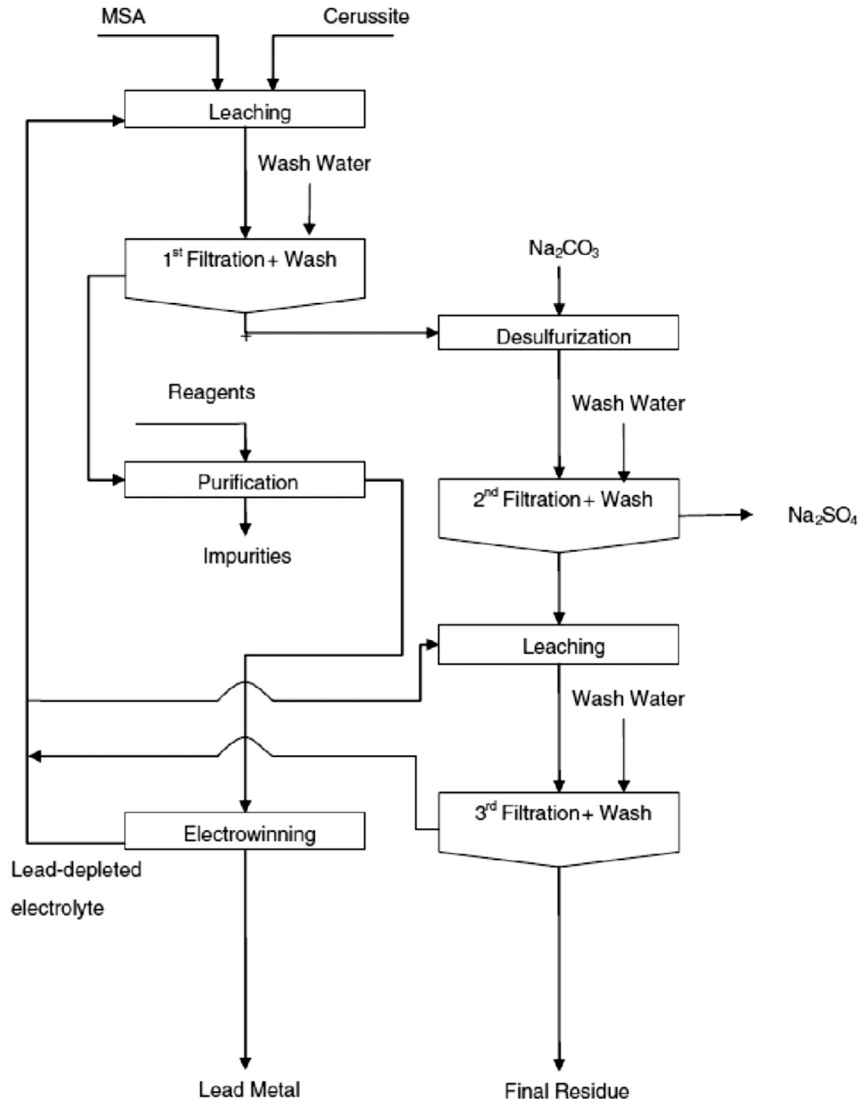


Fig. 11. Proposed flowsheet for lead recovery from cerussite concentrate in MSA based solution [70].

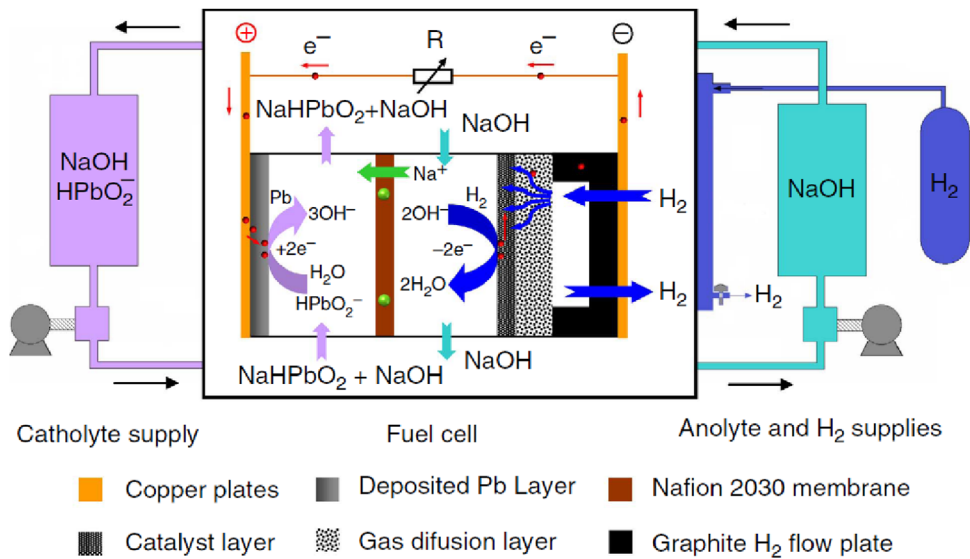


Fig. 12. The schematic of the H_2 - PbO fuel cell.

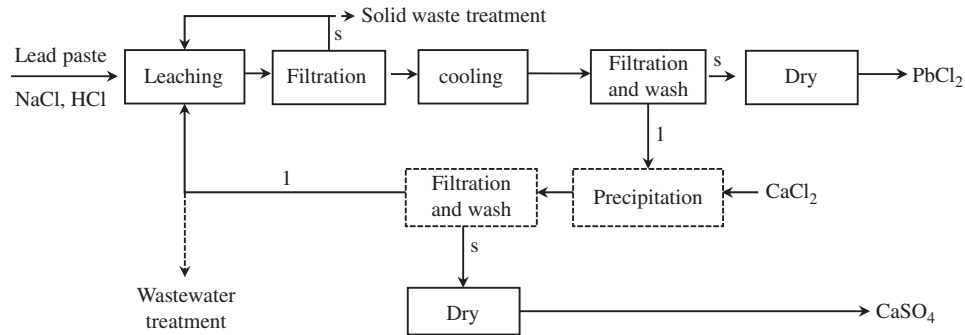


Fig. 13. Flow diagram of the chloride method.



By this novel method, high-purity lead (with purity of 99.9992%) was obtained with the lead recycle efficiency of 99.5–99.6 wt%. This hydrometallurgical lead recycling route based on the H_2 -PbO fuel has completed in the pilot plant test stage and entered the industrialization promotion period [34,74]. The environmental issues, like the emission of sulfur oxides, nitrogen oxides and lead particulates pollution associated with the pyrometallurgical method were addressed through this route. Furthermore, the electricity is produced in this process with the only by-product of water. However, for long term running plant, the replacement of membrane should also be considered.

3.3.3. Leaching reagents treatment followed by low-temperature calcination procedure

The spent lead paste would be firstly treated with leaching reagents to convert into soluble or insoluble precursors, and followed with further treatment.

Firstly, the lead paste was treated with the solution of sodium chloride and hydrochloric acid, and followed by crystallization and filtration procedure [75–78]. The percentage of sodium chloride was found to have positive effect on the reaction of lead sulfate and dissolution of lead chloride. The leaching efficiency could reach 99.3% at 70 °C for 2 h. Flow diagram of the chloride method is shown in Fig. 13. This processing method provides a new way for lead paste treatment. Furthermore, using sodium chloride as a leaching agent lowers the overall processing cost. However, the concentration of impurities in the obtained lead containing products has not been discussed. Besides, this route was not competent for the conversion of lead paste at a large quantity, because the lead sludge in the factory was agglomerated.

Gao et al. have investigated the solvothermal treatment of PbO_2 in pure methanol at 140 °C, while the main products were determined as mixture of PbO and lead oxide carbonate. The obtained products were then calcined at a temperature of below 500 °C, where the PbO powders were prepared, and the tested batteries made from which showed a high discharge capacity. Based on the previous studies, the mixture of PbO_2 and PbSO_4 in different molar ratios were desulphated and solvothermally processed. Eventually, the calcined products were highly electrochemically active. The flow sheet of the novel procedure for mixtures of PbO_2 and PbSO_4 is shown in Fig. 14 [79,80]. This method can eliminate lead dust and sulfur dioxide pollution, while its energy consumption is lower than the conventional electrolysis route. However, the demand for high temperature and pressure during the solvothermal treatment would set higher requirements for the reactor and technology. A novel route was also proposed by Gao et al. to reproduce new lead acid battery from the spent battery [81,82], which contains the separation step and subsequent production of the novel positive and negative active materials at the temperature of below 700 °C. The comparison between the recycle route and

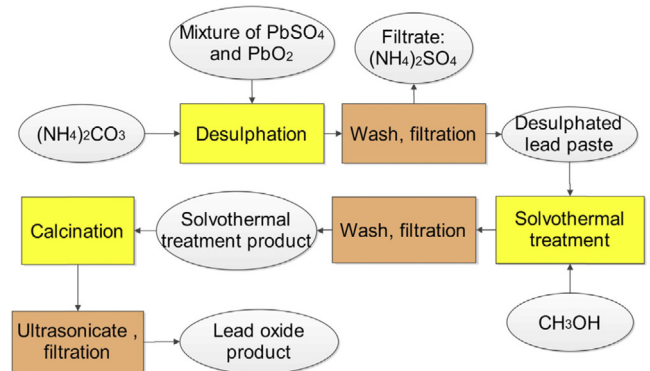


Fig. 14. Flow sheet of the novel procedure for mixtures of PbO_2 and PbSO_4 . [79].

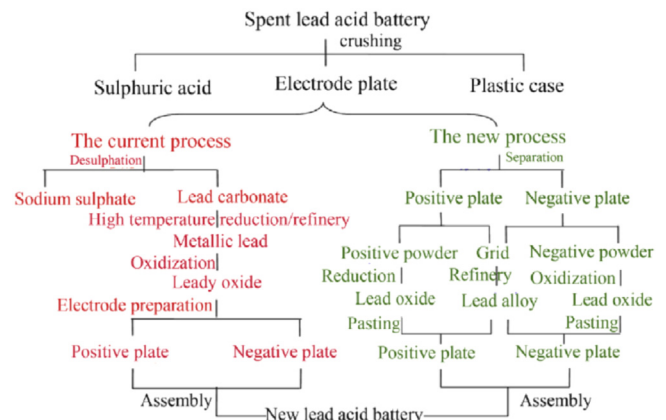
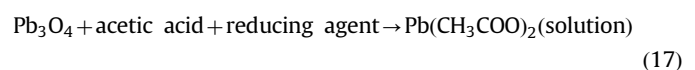


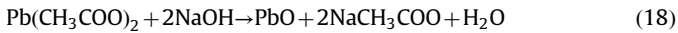
Fig. 15. The comparison of the recycle route with the current one.

the current one is shown in Fig. 15. It is quite difficult to separate positive and negative electrodes from the spent lead battery directly, especially in large-scale industrial plant.

The recovery of lead oxide products from lead acid battery pastes was investigated through the preparation of lead carboxylate [83–86]. The spent lead pastes were treated with alkaline hydroxide consisting of sodium hydroxide and potassium hydroxide at the pH of at least 12 at a temperature of 60–70 °C. After the desulphurization reaction of lead sulfate, Pb_3O_4 was obtained in the alkaline hydroxide treating step by filtering. After washing, the obtained Pb_3O_4 was further reacted with carboxylic acid and reducing reagents. The reducing agent was aldehyde for the Pb_3O_4 conversion. The reaction involved in this process is shown as follow.



The reaction temperature of obtained filtrate with alkaline hydroxide was around 50–100 °C, while the PbO was recovered from the procedure. The reaction is given as Eq. (18). The flow sheet of the recovery process is shown in Fig. 16.



Generally, this process was a meaningful attempt for recovery of PbO through preparation of lead acetate. Considering the recovery ratio (> 90%), this novel method may not be feasible for the industrial plant. Additionally, there still remains some lead which would not enter the next step in the filtration procedure.

Ma et al. [87] decomposed the desulphurized lead paste through vacuum thermal process under high temperature, while the lead carbonate could be easily converted into lead oxide. The lead oxide would be reduced into fine lead in the vacuum thermal process. The recovery ratio of spent lead paste and the purity of lead are both effective.

Kumar et al. [14–17,88–96] have pioneered sustainable paste to paste recycling method, where the spent lead acid battery paste

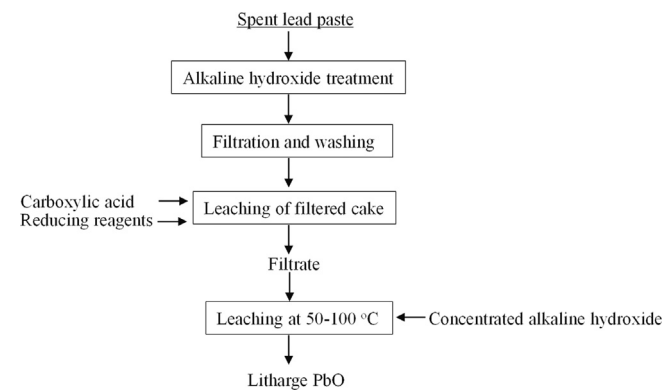


Fig. 16. Flowsheet of the recovery of lead oxide researched by SA Kinsbursky [86].

was directly converted into the novel lead oxide paste for the new lead-acid battery. In this green route, spent lead paste was treated with an aqueous solution to generate a lead containing precursor. The flow sheets of our two different leaching procedures by Kumar and Yang are shown in Fig. 17.

After the calcination of lead containing precursor at a low temperature in air or nitrogen atmosphere, the ultra-fine lead oxide powder would be obtained. The morphology of calcination products changes into spherical structure as shown in Fig. 18 [90]. The spherical structure of calcination products was mainly the morphology of PbO and Pb products. The synthesized lead oxides from the calcination procedure were used as active material in the lead acid battery assembly. The lead acid battery assembly procedure is shown in Fig. 19 [97–99]. The results reveal that the lead oxide obtained at 375 °C shows good electrochemical performance and initial capacity [97–99]. This hydrometallurgical route based on paste to paste method has already been in the pilot plant test stage. The content of sulfate in lead citrate precursors prepared by this pilot plant test was measured less than 0.2 wt%, indicating a complete conversion of lead sulfate in spent lead paste. Ma et al. also apply the oxalate and sodium oxalate in the leaching procedure, while precursor of PbC_2O_4 could be obtained. The lead oxides synthesized from calcination of precursor could be used in assembly of new battery [100].

Lastly, some novel route such as mechanochemistry route was also applied in the lead recycling from secondary lead, i.e. waste CRT glass. For the process, the Pb–O and S–S bonds broke down, while lead sulfide formed during the mechanochemistry operation, which could be gathered and recycled. This novel method was also an good attempt in the secondary lead recycle area [101].

3.3.4. Technology needed to be improved

For the impurities in the spent lead paste may easily enter into the recovery system, the removal of impurities, such as iron, antimony, barium sulfate, etc. still need to be discussed. Without

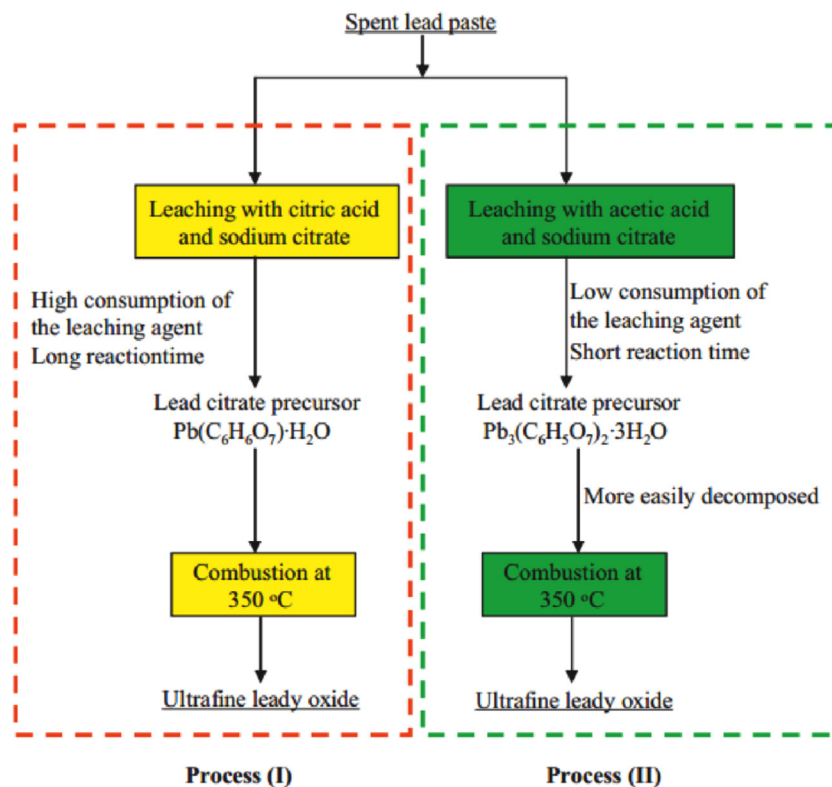


Fig. 17. Flow diagram of two different leaching procedures.

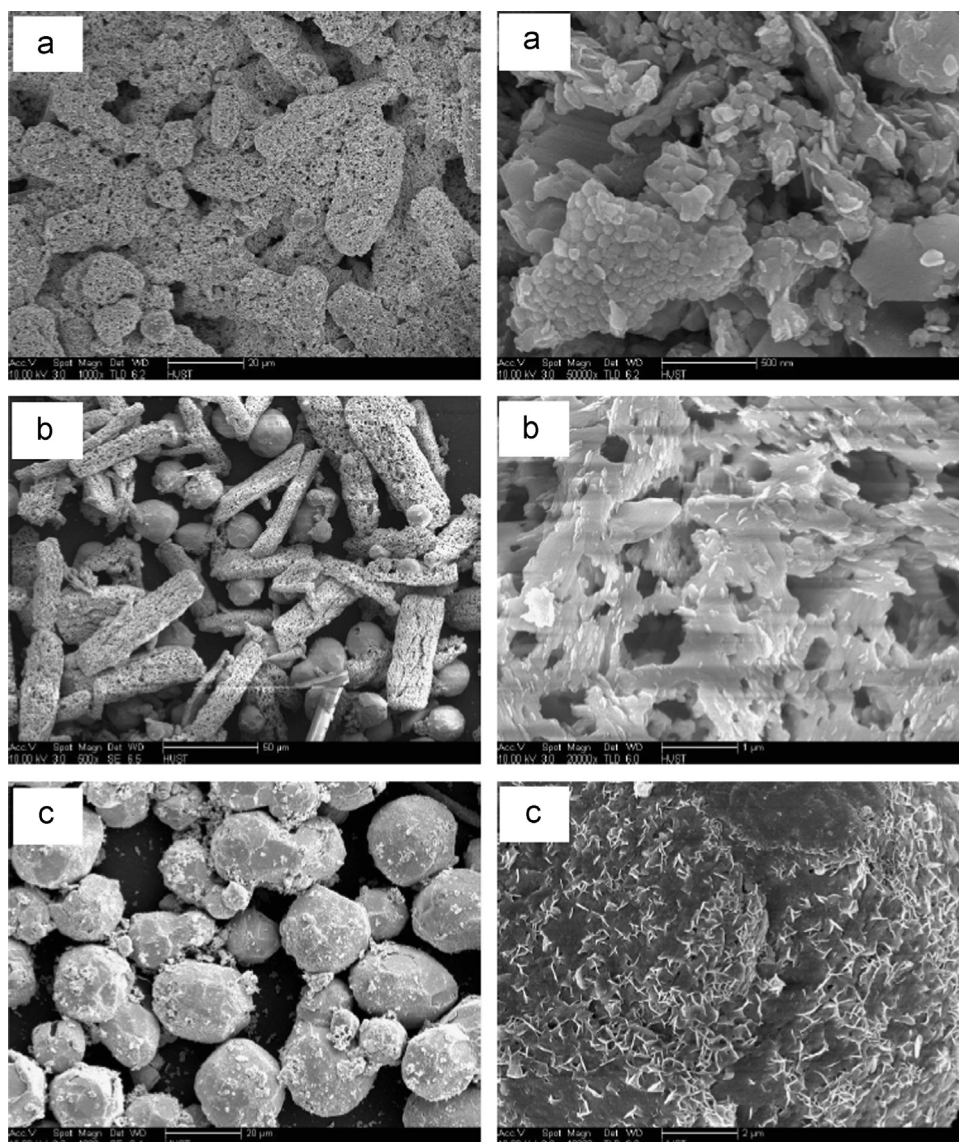


Fig. 18. SEM images of calcination products at different temperature for 1 h in air: (a) 300 °C, (b) 350 °C, and (c) 450 °C [90].

proper removal of the impurity metals, the electrochemical properties of the final lead products would be invariably decreased for the existence of the harmful impurities.

Furthermore, the reuse of filtrate containing unreacted leaching reagents also draws increasing attention in this hydrometallurgical route. In general, the excessive dosage factor of leaching reagents would lead to presence of unreacted reagents, which was then filtered for further treatment. The run cost would increase by a large margin if the reuse of the unreacted leaching reagents were not taken into consideration.

4. Prospect: from spent lead-acid battery to high-performance battery

Considering the further application of lead-acid battery in hybrid electric vehicles [HEVs], more and more battery researchers and engineers are trying to improve its energy and power performance [102–108]. The lead acid battery would be a more achievable and plausible alternative choice if the high-performance and light-weight lead-acid batteries could be developed. It would be an

open challenge for preparation of high-performance battery directly from spent battery.

It is suggested that the addition of carbon materials can improve the electronic charge transport in lead-acid battery, thus, improving their power density and capacity. The promotion of lead-acid battery adoption in hybrid electric vehicle highly requests improving their energy density and recharge availability [109]. An important issue of lead-carbon battery that needs to be focused on is the adhesion properties between the negative active lead material and carbon additives. Besides, it is also important to reduce the cost of lead carbon batteries. The fact should be acknowledged that the preparation of high-performance battery from the secondary lead was a prior approach for the lead recovery. What's more, the replacement of the lead-alloy grids with ultra-light new materials could lighten the mass of the battery, which would increase the energy density of the battery by a large margin than current batteries. The light materials grid such as lead foam grid [110–112], carbon honeycomb grid [103,113], carbon foam lead-acid battery grid [114–117], etc. were recently proposed for the reduction of the battery support material. It is an open challenge to combine novel lead oxide materials recovered

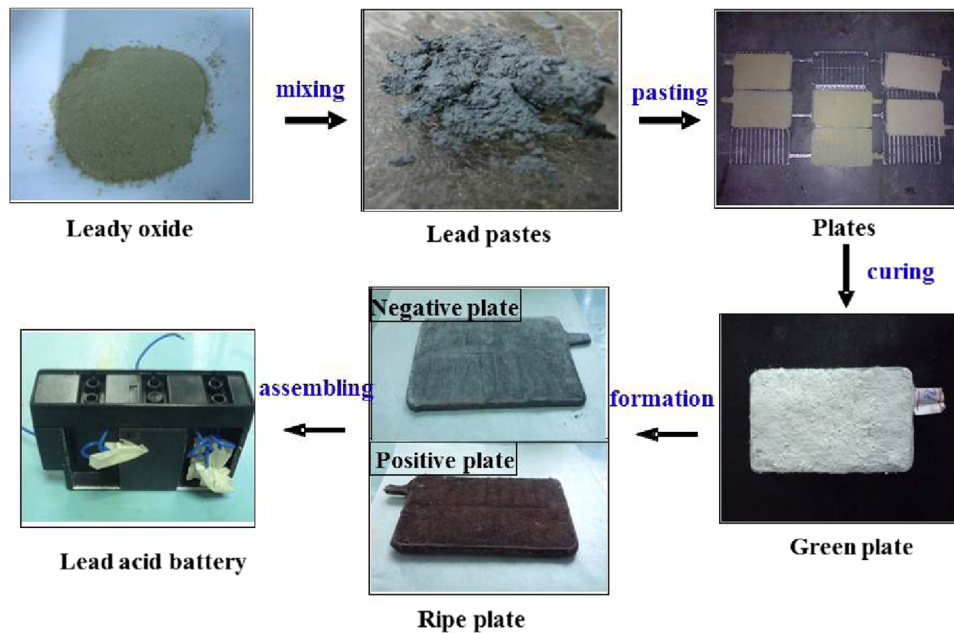


Fig. 19. Schematic diagram of the assembly of lead acid battery [97].

from spent lead pastes with the smart grid for meeting the requirement of high-performance battery.

Based on the above consideration, the preparation of lead negative active material consisting carbon in the recycle of spent lead paste through a green recovery route, followed by negative plate preparation and battery assembly, should be a prior choice for clean recovery of spent lead-acid battery and manufacture of new battery with high-performance.

5. Conclusions

- (1) The secondary lead dominates much of the lead market all over the world, especially in developed countries or areas. Presently, the secondary lead recycling is still associated with pyrometallurgy route. Despite the lead smelting route makes significant progress in energy conservation and environmental release, the uncontrolled emission of PM_{2.5} containing lead particulates and SO₂ was a major environmental problem, i.e. lead pollution to the human and environment.
- (2) The eco-friendly electrohydrometallurgical technology was developed as an alternative to pyrometallurgical process for the secondary lead recovery during the past 30 years. Due to high operational cost and expensive devices, there is hardly any recycle plants based on electrowinning process with significant capacity. Further development and trials are in the pipeline at the moment.
- (3) Over the past decade, various innovative and environment friendly methods have been proposed and developed for secondary lead production. Though, there are still many areas in these green methods that require further improvement and optimization. However, in term of environment benign and efficiency, these methods are still advanced routines for recovering of spent lead paste in spent/discarded lead acid batteries. The paste to paste method exhibits the most promising applications in recycling secondary lead from spent battery to produce raw lead materials that are suitable for direct usage in new battery production.

- (4) As far as high-performance lead batteries are concerned, secondary lead are cheaper than primary lead resources. Possibly the main challenge would be whether the secondary lead are suitable for the incorporation of carbon materials. It is also interesting to investigate whether carbon materials can be produced as a by-product of secondary lead recycling from spent batteries. The green routes of secondary lead recycling from spent lead-carbon battery in the future will also be an interesting research area for many years to come.

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