Developments in electrochemical processes for recycling lead-acid batteries

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Abstract

The lead-acid battery recycling industry is very well established, but the conventional pyrometallurgical processes are far from environmentally benign. Hence, recent developments of lead-acid battery recycling technologies have focused on low-temperature (electro-)hydrometallurgical processes, the subject of this review, covering modified electrolytes, improved reaction engineering, better reactor design and control of operating conditions.

Keywords

Electrowinning processes; Lead-acid batteries; Battery recycling technology; Pyrometallurgy

Introduction

Production of lead-acid batteries (LABs) accounts for >85% of global lead usage, amounting to ca. 10 Mt a^{-1}. Due to their mature, robust and well-understood chemistry and their ability to deliver bursts of power, necessary for the starter ignition of internal combustion engines, LABs are used in almost all of the world's 1.3 billion vehicles currently in use, and in building back-up power supplies worldwide, accounting for a global industry worth ca. 40 G£ a^{-1}. Furthermore, they are still present in state-of-the-art hybrid and fully electric vehicles due to their position as their established market dominance for 12 V auxiliary power supplies for electronic devices. The continual growth in the number of vehicles and electric bicycles is linked directly to increasing global Pb demand, resulting in an unavoidable increase in spent LABs.

Although recycling of LABs [1–4] already accounts for >85% of the total secondary Pb produced, current LAB recycling practices are dominated conventionally by pyrometallurgical processes [2–4], with high energy consumptions and expensive gaseous and liquid pollution abatement technologies to minimise emissions of highly toxic lead [4–6]. Due to the recent rapid increase in LAB production and consumption with a forecast annual global growth rate of 3.7% [7], the scale of secondary Pb recycling is expected to continue to increase. Hence,

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alternative low temperature hydrometallurgical technologies have been developed to offer efficient and sustainable recycling solutions. This review compares conventional pyrometallurgical technologies for recycling of LABs with present and prospective electrochemical technologies, describing recent progress in electrolyte choice, improved reaction engineering, better reactor design and control of operating conditions. Other hydrometallurgical processes [8–13] based on Pb oxide precipitation and calcination are not reviewed herein.

Conventional pyrometallurgical lead recycling processes

LABs have lead dioxide (PbO_2) film cathodes, sponge metallic Pb anodes, fibreglass mat separators, and aqueous sulfuric acid electrolyte solutions, all contained in polypropylene cases. Prior to metallurgical processing, pre-treatment of end-of-life LABs is carried out by breaking, crushing and physical separation into streams of: polypropylene and plastics (5–12 wt%), sulfuric acid electrolyte (11–30 wt%), metallic Pb grid (24–30 wt%) and Pb oxide/sulfate paste (30–40 wt%). Typically, the plastic materials are recycled, and the sulfuric acid waste is sent to an acid plant for purification. The average mass of Pb paste from one spent LAB is a 6 kg mixture of $PbSO_4$ (50–60 wt%), PbO (5–10 wt%), PbO_2 (15–35 wt%) and metallic Pb (2–5 wt%) [14].

Initially, to avoid SO_2 emissions during ('indirect') smelting, '$PbSO_4$' is de-sulfated by conversion in sodium carbonate solution to '$PbCO_3$', followed by its thermal decomposition at ca. 400 °C, desorbing CO_2, then reduction with coke of the entire mixture to reduce all Pb-containing compounds to metallic Pb. 'Direct smelting', without de-sulfation not only results in SO_2 emissions, but also has higher specific energy consumption and produces Pb dust, ash, and other pollutants, requiring treatment. Even so, direct smelting is still practiced widely, particularly in low-to-middle income countries [3].

In the first stage of secondary smelting, the Pb scrap is reduced by addition of coke in a reverberatory or rotary furnace, operating at 1100–1300 °C. The primary bullion (85–92 wt% Pb) contains low concentrations of Sb, As and Sn, but it can be refined easily to high purity Pb suitable for battery production. In stage two, a secondary lead-antimony alloy (8–10 wt% Pb) is produced from the slag containing all of the alloying elements and impurities. This stage can be carried out in the same vessel after removal of the primary Pb bullion or in a separate small blast furnace [15–17, 18**]. The alloy product requires moderate refining and alloy composition adjustment to form a marketable antimonial alloy. The final slag (1–4 wt% Pb)

can be discarded if the lead content is sufficiently low to be environmentally acceptable. Further details summarising the conventional pyrometallurgical process are shown in Figure 1(a).

Specific environmental pollution phenomena associated with battery recycling, both external and in-plant, have been well described in the literature [3,18**,19]. In particular, pyrometallurgical processes are responsible for significant emissions of heavy metals and acidic gases. The World Health Organisation reports the ambient air quality standard limit of 0.5 µg m^{-3} averaged over one year in the European Union for Pb concentrations in the outdoor environment but it should be noted that this is not a health-based standard. Dust emissions containing Pb particulates constitute threats to humans, animals, soil and drinking water, particularly in the vicinity of Pb smelting plants, which are often located near large urban centres, to minimise costs associated with transporting large amounts of scrap [19]. Despite the progress of Pb smelting technologies, there is a need for the development of cleaner and more efficient secondary Pb processes, with lower costs and energy efficient methods for recovering Pb from end-of-life batteries.

Chemistries for lead electrowinning

Pyrometallurgical smelting processes dominate the secondary Pb market and presently account for >90% of the Pb recovered from end-of-life LABs. However, over the years, many (electro-)hydrometallurgical processes have been proposed, involving electrolytic conversion of dissolved Pb^{II} to high purity Pb cathodes, as they are considered to have less negative environmental impact, due to low operating temperatures, minimised dust emissions, acceptable gaseous emissions (O_2 and H_2) and high flexibility. Furthermore, electrochemical deposition can be highly selective, resulting in high purity (>99.9%) metal, so obviating the need for Pb refining.

Conventional (electro-)hydrometallurgical process strategies start with Pb paste de-sulfation, like indirect smelting technologies; sulfur in the paste is converted into soluble sulfates by reacting with Na_2CO_3, $NaOH$, $(NH_4)_2CO_3$ or NaC_2O_4 solutions. Sodium sulfate, Na_2SO_4, by-products are used for other industrial applications. The insoluble product $PbCO_3$, $Pb(OH)_2$, or PbC_2O_4 is collected and converted to a Pb^{II}–containing solution by leaching with acidic solutions such as HCl, H_2SiF_6 or HBF_4. The Pb^{II}–rich solution is then electrolysed to produce high purity Pb, which is melted and cast into lead 'pigs' suitable for making new batteries. This process is summarised and compared to the conventional pyrometallurgical process in Figure 1(b).

Intensive research in the 1980s and 1990s led to many piloted technologies such as Revere Smelting and Refining (RSR) [20], Bureau of Mines Process (BMP) [20], FLUBOR [21**,22] and PLACID [23,24] processes. In the mid-1990s, the FLUBOR process [22], developed by Engitec Impianti, was piloted at 45 kg_{Pb} day^{-1} at Asarco's East Helena Lead Smelter using granulated lead bullion and successfully produced 99.9% pure lead sheets. In 2014, a demonstration plant reported production of 2000 t_{Pb} a^{-1} [25**]. The PLACID process [23,24], led by Téchnicas Reunidas, was piloted during 1995–1996, to produce 400 kg_{Pb} day^{-1} with an average purity of 99.995% . It was envisaged that a production version of this process would have a minimum output capacity of 730 t_{Pb} a^{-1} $cell^{-1}$ with current densities of 1000–1200 A m^{-2} and a mass-specific electrical energy consumption of 0.9 kW h kg_{Pb}^{-1}. The CLEANLEAD process [26] was piloted with a plant capacity of 400 kg_{Pb} day^{-1}; battery paste leaching and subsequent lead electrowinning were both carried out in alkaline media. Current densities of 650 A m^{-2} allowed an energy consumption of around 0.6 kWh kg_{Pb}^{-1} with charge yield close to 100%. More recently, Aqua Metals Inc have developed the AquaRefining^{TM} technology [27,28*], using an aqueous solution of methanesulfonic acid (MSA) and ethylenediaminetetraacetic acid (EDTA). This modular technology enables continuous Pb recovery at a rate of 2.5–3.0 t_{Pb} day^{-1} $module^{-1}$.

A laboratory scale process has been reported [29] for the recovery of electrolytic Pb powder from battery sludge by direct electrorefining in titanium net basket anodes immersed in an acidified leach liquor containing 1.24 wt% HCl acid and 2.2 wt% Pb^{II}. The effects of current density, temperature and concentrations of Pb^{II} and MSA, have been reported [30] on electrorefining of Pb from MSA media; 99.99% purity Pb was produced with > 0.99 charge yields and specific electrical energy consumptions < 1.1 kW h kg_{Pb}^{-1}.
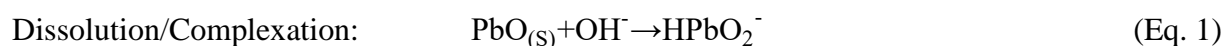
Despite the apparent success of Pb electrodeposition from aqueous solutions, it is difficult to avoid its dendritic growth on cathodes. Hence, room temperature ionic liquids (ILs) have been explored as alternative electrolytes for Pb electrodeposition due to their unique physicochemical properties: wide electrode potential windows, good thermal stability, low melting points and high ionic conductivities. Wang et al [31] investigated the electrodeposition of Pb on Au from an imidazolium chloride-AlCl$_3$ mixture, reporting Moiré-like patterns of Pb adatoms. Katayama et al [32] demonstrated the electrochemical separation of Pb from Sn in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and the effect of cathode potential on morphologies. MacFarlane et al [33] researched the electrochemical cycling and deposition morphology of Pb from 1-ethyl-3-methylimidazolium

bis(trifluoromethanesulfonyl)imide, showing compact and non-dendritic depositions. Further, Ru et al. [34–36] explored the use of a urea-based deep eutectic solvent (DES) to deposit uniform sub-micrometre Pb wires, studying the effects of temperature and current density on charge yields, specific electrical energy consumptions and deposit morphologies, while Poll et al [37] demonstrated >99.7% Pb extraction from an ethylene glycol-based DES mixture via electrodeposition. Liu et al [38] and He et al [39] reported uniform, dense and non-dendritic Pb deposition from an urea-imidazolium DES mixture while Liao et al [40*] studied the electrochemical properties of water-insoluble $PbSO_4$, PbO_2 and PbO phases in urea-choline chloride DES mixtures, reporting similar behaviour for all Pb compounds studied. Furthermore, Chen et al [41,42] has demonstrated smooth and uniform Pb deposition from Pb oxides dissolved in a hydrophobic Brønsted acidic amide-type IL, protonated betaine bis((trifluoromethyl)sulfonyl)amide. However, despite being fashionable, the use of ILs also raise problems of availability at scale, cost, chemical stability, recycling and effluent treatment, as well as the question of what anode reaction is possible.

Anodic reaction and reactor designs

Innovations in anodic reaction design

High specific electrical energy consumptions of existing (electro-)hydrometallurgical processes are typically attributed to large cell potential differences associated largely with the anodic reaction, usually oxygen evolution [43]. Pioneering work of Pan et al [43,44**], demonstrated a lead recovery process based on a H_2-Pb fuel cell, in which H_2 gas was fed to the anode to undergo electro-oxidation with OH^- ions to form water, while refined PbO dissolved in heated aqueous NaOH to form $HPbO_2^-$ ions, was fed to the cathode, at which it was reduced to metallic Pb and OH^- ions (Figure 2(a)).

Dissolution/Complexation: $$PbO_{(S)}+OH^-\rightarrow HPbO_2^-$$ (Eq. 1)

Anode: $$H_2+2OH^-\rightarrow H_2O+2e^-, \quad E^0 = \text{-0.828 V vs SHE}$$ (Eq. 2)

Cathode: $$HPbO_2^-+H_2O+2e^-\rightarrow Pb_{(s)}+ 3OH^-, \quad E^0 = \text{-0.531 V vs SHE}$$ (Eq. 3)

High purity metallic Pb (99.9992%) was obtained with yields > 99.5%. In principle, a positive standard potential of 0.297 V gives a spontaneous reaction between H_2 and $HPbO^{2-}$ ions to produce Pb, water and electricity. This new process was shown to consume 1/2 and 1/3 of the specific energy of a conventional pyrometallurgical and (electro-)hydrometallurgical process,

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respectively. This process has completed the pilot plant test stage and entered a small capacity industrialisation phase led by Chaowei Power [5].

Innovations in reactor design

The (Flakes Auto-Stripping Technology) FAST® Pb process [25**] developed by Engitec (www.engitec.com) is a new electrochemical approach based on a chloride electrolyte in a high productivity flow cell. This process utilises an ammonium chloride leachant after Pb paste de-sulfation. Hydrogen peroxide is used to dissolve PbO_2 reductively by:

$$PbO_2 + 2H^+ + H_2O_2 \rightarrow Pb^{2+} + 2H_2O + O_2 \qquad \text{(Eq. 4)}$$
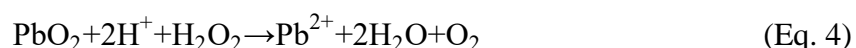
The electrowinning process takes place in a flow cell in which the solution is passed between two parallel plate electrodes (Figure 2(b)) at a high linear velocity, to shear lead flakes (dendrites) produced at the cathode:

$$NH_4PbCl_3 + 2e^- + 2H^+ \rightarrow Pb_{(s)} + NH_4Cl + 2HCl \qquad \text{(Eq. 5)}$$

Unlike other chloride electrolysis systems, chlorine gas bubbles are not evolved at anodes, as any chlorine generated is converted rapidly by a coupled chemical reaction with ammonium ions [45] present in the anolyte to metastable chloramines and then to nitrogen gas:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{(Eq. 6)}$$

Immediately followed by overall reactions such as:

$$3Cl_2 + 2NH_4^+ \rightarrow N_2 + 8H^+ + 6Cl^- \qquad \text{(Eq. 7)}$$
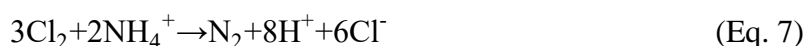
This type of reaction limits concentrations of active chlorine that would otherwise be reduced preferentially at cathodes, decreasing charge yields for Pb recovery. To increase Pb^{II} solubilities, the system is operated at temperatures in the range of 65–80 °C. The cathode is operated close to transport limited current densities to produce highly dendritic deposits that are easily stripped hydrodynamically from the cathode continuously. Turbulent flow through the electrochemical reactors, N_2 bubble generation at the anode, as well as an air sparging system increase mass transport rates and allow current densities of up to 10 000 A m^{-2} to be achieved. The solution leaving the reactor contains the ammonium chloride to be used as the leachant, so closing the electrolysis circuit. To decrease ohmic potential losses in the electrolyte, the electrode gap is ca. 10 mm, but this is wide enough to avoid lead dendrites growing on the cathode from contacting the anode and re-dissolving. The cell potential difference, *U*, is typically 3.0–3.1 V; with cathodic charge yields, of >0.85, specific electrical energy

consumptions, $w_{Pb}^e/kW\ h\ t_{Pb}^{-1}=\frac{2F}{\Phi_{Pb}^e}\frac{U}{3.6M_{Pb}}\approx950$, where Φ_{Pb}^e is the overall charge yield, F is the Faraday constant and M_{Pb} is the molar mass of Pb.

Challenges with the development of industrial scale lead electrowinning processes

Compared to pyrometallurgical Pb recycling processes, electrowinning processes are still considered to be less economically favourable and are typically associated with high operating costs due to the chemical reagents necessary for Pb paste dissolution, as well as significant capital costs with high equipment replacement rates due to corrosion of metallic components in the electrowinning equipment. Additionally, a major challenge to the technological development of Pb recycling processes is the existence of many insoluble/partially-soluble phases of Pb, limiting production rates and capacities. Anode reaction choice/design is also of significant academic interest, as avoidance of PbO_2 deposition is challenging but significantly important to the deployment of any electrowinning technology. We note here that PbO_2 could be a useful secondary product but has rarely been implemented.

Anode materials are also typically costly and may have short life-spans. Further, toxic materials employed in these processes impose significant health risks to workers. Hence, (electro-)hydrometallurgical processes have not been adopted widely by existing industrial plants even after 30 years of research and development, despite growing interest and new investments into this area.

Current practices in the UK metal industry are classified as energy intensive industries and account for 40% of the UK's carbon emissions from businesses and the public sector. Consequently, they are susceptible to policies aimed at moderating climate change, potentially making the UK Electrical and Electronic Engineering industries sector uncompetitive with the rest of the world, particularly as there is yet no common global standard to reduce carbon emissions and with high and rising energy costs. Consequently, it is anticipated that such industries would be more inclined to adopt greener recycling solutions in the near future.

Conclusion and Perspective

Recycling of spent LABs is well-established, due to their simple structure and chemical composition. The purities of the recycled and refined Pb compounds are high enough for their re-use in new LABs, making the recycling process essential to the LAB circular economy. Although the LAB recycling industry enables 99% of all batteries to be recycled, end-of-life

LAB recycling is also globally the most polluting industrial process [18**]. The effective management and development of the LABs recycling sector is significantly challenging, due to the presence of non-regulated informal recycling. While rates of Pb exposure and release are highly controlled and regulated in developed countries, these rates are considerably higher in low-to-medium income countries. This has resulted in lead exposure and poisoning; e.g., 10 major lead poisoning incidences have been reported in China over the last decade [19], while an assessment of workers in a Kenyan smelter revealed blood lead levels over six times higher than normally acceptable [18**]. Hence, there is an urgent need for research and development of novel and improved recycling processes that are energy efficient, environmentally benign and economical, thereby achieving sustainability of battery technologies.

Conflict of Interest

The authors have no conflicts of interest.

Acknowledgements

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** This articles reports a new green lead-acid battery recycling process utilising the 'so-called' H_2-PbO fuel cell. Major advantages of such a process include eliminating Pb vapour and slag release, unlike pyrometallurgical processes, and eliminating the use of toxic chemicals required for most hydrometallurgical processes. This new process also produces electricity and can also be applied to other metal/battery recycling process design.

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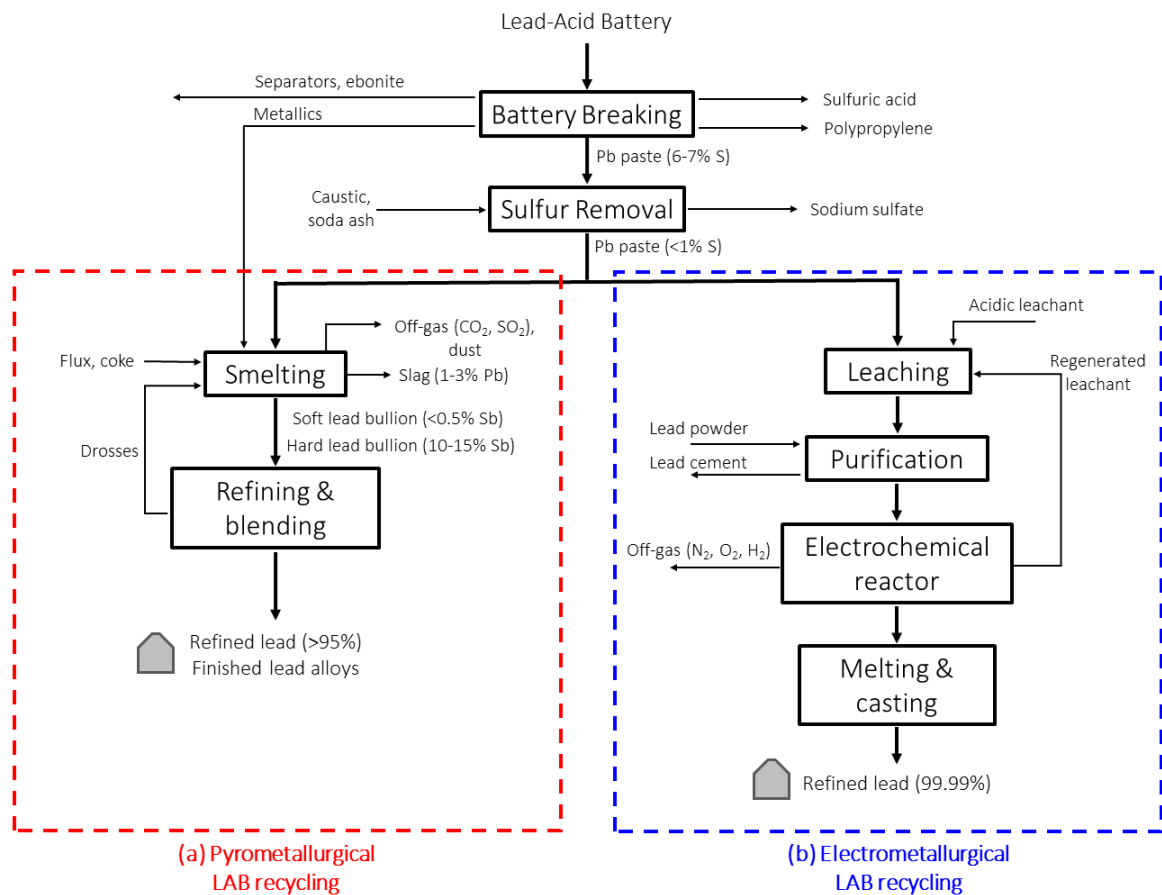
Figures

Figure 1. Schematic showing the conventional (a) pyrometallurgical versus (b) (electro-)hydrometallurgical spent lead-acid battery recycling process. (print in colour)
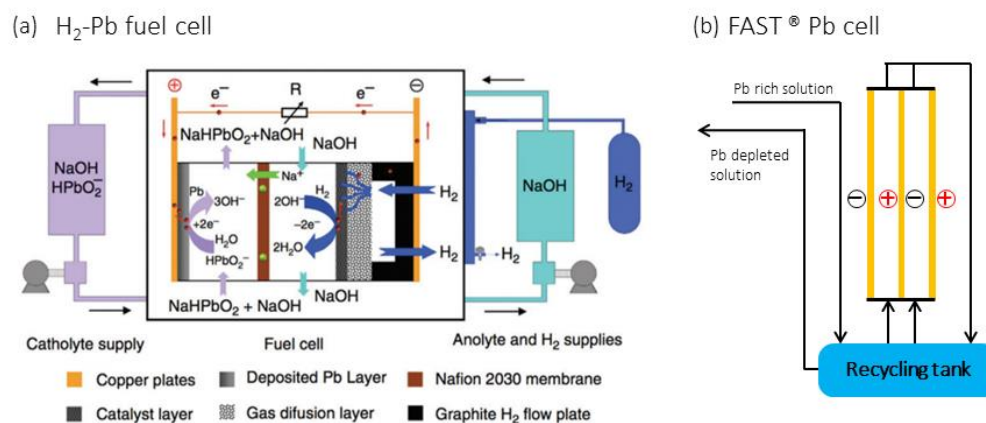

Figure 2. Schematic of the (a) H_2-Pb fuel cell (reprinted with permission from [44**]) and (b) FAST® Pb electrolytic cell (adapted from [25**]). (print in colour)