

FUNDING OPPORTUNITY ANNOUNCEMENT:
Deep Eutectic Solvents for the Recycling of Lead Acid Batteries
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Summary of Abbreviations:

DES – Deep Eutectic Solvents

HBA – Hydrogen Bond Acceptor

HBD – Hydrogen Bond Donor

IL – Ionic Liquid

LAB – Lead-Acid Battery

PM_{2.5} – Particulate matter less than 2.5 microns in diameter

Type III DES – Deep eutectic solvent made with Quaternary Ammonium Salt and hydrogen bond donor

Type IV DES – Deep eutectic solvent made with metal halide and hydrogen bond donor

ULAB – Used Lead Acid Battery

1.0 Introduction

Lead-Acid Batteries (LAB) are widely used in society, particularly in automobiles as the source of energy to start a vehicle. The closed-loop, direct recycling system for LAB is a mature process, with high recovery of metallic lead and high proportion of used lead acid batteries (ULAB) recycled [1]. In the USA, 99% of ULAB are recycled, and secondary lead is the major source of lead in many areas of the world.

1.1 Existing Recycling Process

The simple construction of LAB is critical for the existing recycling model. The high proportion of lead in LAB leads to a financially viable model, and low dispersion of the material reduces recovery costs. One major success of the automotive industry is the first stage of recycling – collection and transportation of ULAB. In industrialized countries, the recycling process is generally standardized. The mechanical stage of the process includes emptying the acid, crushing the batteries in a hammer mill and separation of materials using gravimetric and hydrodynamic devices. The battery is separated into lead pastes, lead grids, sulfuric acid and plastic components. The plastic is recycled by conventional methods and the recycled plastic is often used for new lead batteries. The sulfuric acid is neutralized by sodium or calcium hydroxide, and the salt byproducts sold. Lead grids are metallic lead and can be recast, and the lead paste is smelted before recasting [2]–[4]. **Error! Reference source not found.** shows the typical LAB recycling methods using pyrometallurgy. The sulfur removal stage is an additional step not always utilized.

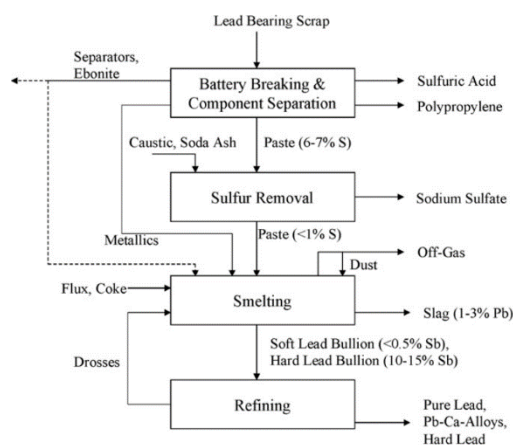


Figure 1: A typical flow diagram of secondary lead recycling [2]

2.0 Impact

The concept explored will address high global warming potential of the smelting phase of LAB recycling, as shown in Figure 2, by proposing a hydrometallurgical method to replace the existing pyrometallurgical procedure. Successful implementation of novel or improved recycling methods in the automotive industry have widespread impact, and despite the arrival of the electric vehicle era, LAB remain the battery of choice in the automotive industry [5].

2.1 Lead Emissions

Lead is a prevalent pollutant that acts as a cumulative toxicant. Its multigenerational impact has devastating impact in low- and middle-income countries. In a 2020 announcement by Pure Earth, the world's leading non-profit on toxic pollution, lead was identified as a leading priority to address [6]. More than 800 million children worldwide have lead concentration of above 5 micrograms per deciliter – resulting in permanent brain damage and reduced IQ by 3-5 points. The economic impact on countries where such IQ loss is experienced is estimated at \$1tn per year [6]. There is only limited data on many of the complex biological and

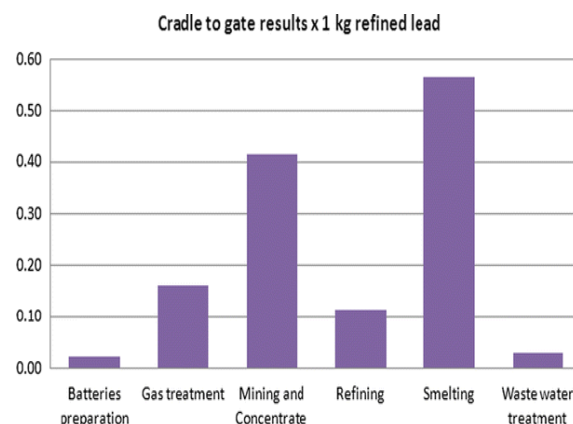


Figure 2: Cradle-to-gate results for lead production LCI in terms of global warming potential [14]

biochemical mechanisms behind the health impacts of toxic pollutants and this gap prevents researchers from truly grasping the scope of the health effects of pollution. Exposure can arise from all parts of the recycling process, from dust generated during milling, fumes produced from smelting, and contaminated electrolyte being spilled into soil, water and wastewater.

2.2 Priority Research Directions

This funding opportunity will focus on new methods of reducing both lead emissions and greenhouse gas emissions by removing the major emission stage in recycling process. The proposed research would replace smelting with a hydrometallurgical process utilizing novel deep eutectic solvents. Successful implementation of the project would further knowledge on the interaction mechanism of lead compounds with deep eutectic solvents. This knowledge would have applicability to LAB recycling, allowing for advancements of the mechanisms to pilot and industrial scale. Emerging research on DES shows promise and demonstrates applicability in both LAB recycling as well as in LAB construction as electrolytes, though applications such as redox flow batteries are beyond the scope of the proposed research.

3.0 State of the Art

3.1 Pyrometallurgy

The practice utilized today in LAB recycling is smelting of lead, a pyrometallurgical process of melting the lead paste, a mix of lead sulfate (60 wt%), lead dioxide (28 wt%), lead oxide (9 wt%), and a small amount of metallic lead (3 wt%) in a furnace at around 1100 °C [3], [5]. The slag produced during smelting becomes a problem for its high lead concentration and reactivity and is often treated with iron in the furnace. The generation of PM_{2.5} is also a concern associated with smelting and is a key pollutant alongside sulfur dioxide and carbon dioxide.

3.1.1 Smelting Kinetics

The existing process for lead smelting has unfavorable carbon dioxide formation. Due to the role of carbon in reducing the lead paste to form metallic lead, carbon dioxide emissions are inherent in the process and end-of-pipe solutions to carbon abatement are the only current proposed solution for reduction of emissions. Ellis et al. propose kinetic models utilized in industrial practices [2].

3.1.2 Industry Practices

In current LAB recycling facilities, emission reduction methods are mostly end-of-pipe which avoid addressing the issue of the creation of pollutants; rather, emissions are captured before release into the wider environment. The processes currently meet sulfur dioxide limits, but as these limits tighten with global emissions targets, the processes must improve.

3.1.2.1 Flue Gas Treatment

Flue gas treatment acts to abate sulfur dioxide emissions by reaction of the sulfur dioxide in the flue gas from the furnace with sodium carbonate. The thermal decomposition of sodium bicarbonate produces sodium carbonate in a very active form which, with fast kinetics, reacts with the sulfur dioxide in the hot gas, producing sodium sulfite and then, by oxidation with the air, sodium sulfate. This reaction can also proceed in aqueous solution where the flue gas is dissolved producing water with high concentrations of sodium sulfite. Sodium sulfate is a commodity chemical which can be sold as a byproduct [2].

3.1.2.2 Hydrometallurgical Paste Desulfurization

The paste desulfurization process converts lead sulfate to lead carbonate, hydroxide or hydrocarbonate by reaction of the paste with aqueous sodium hydroxide or sodium carbonate solutions. The lower solubility products of lead carbonate or hydroxide enable such a process. The degree of desulfurization is 94-96% for well optimized processes [7].

3.2 Electro-Hydrometallurgy

The field of research into electro-hydrometallurgy processes is growing, most popularly with electrowinning. Such techniques have reduced emissions compared to smelting techniques, though high energy costs hinder smaller scale projects. Some processes have utilized strong acids and still requires remelting and recasting [4]. Successful examples have utilized leaching with an acid solution after the paste desulfurization and the lead-rich electrolyte then treated with electrowinning.

3.2.1 PLACID Process

Perhaps the most promising hydro-metallurgical process was the PLACID process. With operational pilots in Spain in 1996, the process achieved high purity lead ingots with no greenhouse gas emissions. The main waste product was gypsum, and a maximum operational temperature of 80 °C resulting in no lead fume emissions. The industrial scale-up of the process was hindered by high energy costs of 1300 kWh per ton of lead produced and industry lock-in to pyrometallurgical methods [8].

4.0 Innovation

The work proposed is to utilize the field of Deep Eutectic Solvents (DES) for lead acid battery recycling. The term deep eutectic solvents refer to “a mixture of Lewis and Brønsted acids and bases which significantly reduce the freezing point compared with those of the components” [9]. DES have particular relevance in electrochemical applications due to high conductivity and tunability, since discovery, they have demonstrated promising properties, particularly in the replacement of ionic liquid (IL) solvents. The classification of DES is by constituent components of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), and the proposed research will focus on type III and type IV due to the limited solubility of lead in aqueous solutions and existing successes of type III & IV DES. The scope of the proposal will not exclude type V DES though there is an unlimited amount of type V DES with no constraints on components, so focus should remain on type III & IV.

4.1 Proof of Concept

Existing research into DES applied to lead recovery has been limited. Liao et al. evaluated choline chloride/urea in 1:2 molar ratio, a common type III DES. Findings included a solubility of greater than 75 mM of lead paste compounds in the DES, as well as activation energy terms for the diffusion of PbSO_4 and PbO_2 in choline chloride/urea and achieving electrodeposition of lead. Understanding of the speciation and knowledge of the formation of Pb(II) was limited [10]. Ballantyne et al. conducted early investigations into DES Ethaline 200 and its suitability as a solvent in lead recycling. Ballantyne concluded the findings were promising with proof of concept with lead deposition conducted [5]. Scope of the investigation was limited to a single type III DES though provided impactful insight and proof of concept.

4.2 Proposed Model

The proposed work includes utilization of computational methods to identify and model behavior of type III & IV DES across a range of electrochemical conditions and evaluate lead solubility. Candidate solvents will have sufficient lead ion solubility and allow for electrowinning resulting in synthesis of metallic lead deposits. Following demonstration by computational methods, laboratory studies evaluating feasibility of large-scale implementation will occur, optimizing coulombic efficiency by evaluating both potentiostatic and galvanostatic electrodeposition for high purity lead.

5.0 – Risks and Challenges

Lead-acid batteries are the established 12 V power supply in cars, and this is expected to remain as the transition into the electric vehicle era continues [5]. As such, improvement to the LAB recycling process is crucial, but time scale could prove challenging. From the proposed research to process conception and implementation in industrial practice, accelerated development would be required to ensure successful execution of DES recycling before the industry advances battery technology beyond lead-acid batteries. Despite time scale challenges, furthered knowledge on DES could provide insightful findings for all heavy metal purification and recycling processes, further understanding on DES thus reducing reliance on the current standard – expensive IL laboratory solvents. The major risk involved is utilization of DES. With emerging fields of research, there is inherent risk that proposed methods have oversights. Reviews performed indicate a growing base of knowledge on DES, and early observations indicate potential for the work proposed [5], [9]–[13]. The large number of candidate DES in the type III & IV categories will generate large datasets to analyze likely increasing uncertainty of the model. Computational methods such as utilization of neural networks propose promising methods to observe non-linear trends in lead ion behavior in solutions [11]. Such methods of computational analysis provide valuable tools to direct the researcher into initial promising candidate solvents, but the risk of futile solvent performance due to computational methods being trained on insufficient data could exist, and be limited by, the current understanding of DES. Existing LAB recycling is limited by technology lock-in, and perhaps the overarching risk is the economic practicability of proposed results is not feasible. A key selection criterion for DES was low costs, but traditional challenges with electrowinning processes including high energy costs may remain. This should remain a focus throughout the process where energy costs are minimized where appropriate.

6.0 – Project Plan

A typical project plan would be proposed. Firstly, a thorough literature review would be conducted to understand existing DES and influence of each component, as well as lead characterization techniques. Given the criterion for DES, a comprehensive component list of Lewis and Brønsted acids and bases, or more generally of HBD and HBA would be collected. At this stage, the behavior and interaction of HBD and HBA are the area of interest and machine learning can accelerate the process to identify relevant DES for lead. It would be suggested that Monte Carlo simulations, artificial neural network using Monte Carlo cross validation or kernel ridge regression are used to model and identify relevant DES with optimal ratios of components. Binary components should be evaluated but there should be no requirement for equimolarity. A shortlist of components should be generated which advance to laboratory testing. At laboratory stage, candidate DES should be tested for lead solubility, and electrodeposition evaluated, and mechanism of interaction proposed. Feedback into the machine learning model should be ongoing with laboratory findings. Testing of DES would be important, observing electrochemical properties on the interaction with lead. Influence of additives should be evaluated, which alter electrochemistry of DES including ionicity. Finally, a mechanism of interaction of a final type III or type IV DES with PbSO_4 , PbO_2 and PbO should be proposed, with optimal conditions for maximal electrodeposition of Pb during electrowinning. Research beyond the scope of the proposal will include scale-up procedures to utilize knowledge found on DES for LAB recycling process, including evaluating the interaction of identified DES with common ULAB impurities. Computational methods findings could be used initially to better understand the mechanism of DES interaction with lead compounds, and perhaps steer focus into further development of appropriate DES for applications beyond lead into other heavy metals.

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