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MORE ENVIRONMENTAL FRIENDLY METHOD OF LEAD RECYCLING FROM WASTE BATTERY PASTE – AN ELECTROCHEMICAL INVESTIGATION

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Abstract

Some polyamines can be used to dissolve many heavy metal compounds due to their complex forming capacity with metal cations. In this study we use an amine as a ligand in lead recycling from battery paste by electrodeposition in order to replace pyrometallurgy – the most popular but polluting technology in Vietnam. After conversion waste battery paste into solution the electrochemical reduction of lead ions on stainless steel electrode was studied using linear and cyclic voltammetry. Voltammetry measurements showed that there are two reduction reactions in studied solutions and stainless steel can be used as a cathode in the electrolysis process.

The preparative electrolysis was conducted in the electrolytes composed of chelating agent and lead species obtained from battery paste dissolution. Electrowinning experiments with stainless steel cathode and graphite anode at various conditions of current density (from 5 to 30 mA/cm²), ligand concentration (150 – 180 g/L) showed that the current efficiency of lead deposition was high and the cathode potential values were unchangeable during 4-hour electrolysis. From studied conditions some optimal (in ligand concentration, current density, additives content etc...) for lead deposition quality were indicated as well.

Key words: battery paste, electrodeposition, lead, recycling and voltammetry

Introduction

Although many secondary batteries with higher capacity and electrical efficiency as nickel-iron, lithium-ion etc were created still lead-acid battery is the most popular chemical power source and the first choice for automobile industry. Battery industry consumes over 85% of annual lead production of the world.

After service life, about 5-6 years, the batteries must be discarded and become a risk for environment because of their sulfuric acid and lead compounds. The battery grid of lead-antimony alloy is not destroyed during the lifetime of battery and could be easily recycled. Meanwhile the lead paste, more complicated, contains various lead compounds (Table 1) and is the object of nearly all studies in the field of lead battery recycling [1].

In Vietnam the total amount of lead battery scrap is over 10,000 tones per year and ceaselessly increases with augmentation of motor vehicles in use [2].

Table 1: The chemical composition in solid phase of Vietnam lead-acid battery scrap

Component		Composition (%)	Total content (%) in solid phase
Metal	Pb	93.5-97.5	31.0 – 40.5
	Sb	2 - 6	
Lead paste	Sb	0.2 – 0.5	43.7 – 54.5
	PbSO ₄	50 - 55	
	PbO ₂	30 - 40	
	PbO	10 - 15	
Others			13.6 – 19.7

The traditional approach of recovering lead from lead acid spent batteries based on pyrometallurgical methods, which is still adopted by large and small sized refining companies, is no longer able to meet the required environmental standards. Experts share the view that traditional plants, even with massive investments in the necessary measures, are still far away of satisfying the statutory requirements related to the release of dust and SO₂ into the atmosphere, to the lead levels in micro and macro climates and to the Pb, Cd and As content of solid waste emissions.

Till now in Vietnam, the battery paste has been recycled in small workshops where lead scrap were reduced with coal at high temperature by pyrometallurgy process. Its product is impure lead metal which need to be refined before used in battery industry. The inconvenience of pyrometallurgy process is the emission of smoke, lead fog and the toxic gases such as SO₂ and CO. The investment of new technologies of pyrometallurgy with exhaust fumes treatment system requires a giant finance and then the price of lead from this technology would not too cheaper than other recycling solutions.

The increasing environmental pressure exercised during the last 20 years, on both primary and secondary lead facilities, has stimulated the research of new and more environmental friendly technologies, such as hydrometallurgy and electrochemistry, as alternative to pyrometallurgy.

In particular, the electrochemical processes, compared to the thermal ones, have some characteristics that make them very attractive as: *high selectivity* (the electrochemical deposition of metal is selective on the metal to be produced); *wastes reduction* (usually no chemicals or massive amount of reactants are used); *no gaseous emission* (in an electrochemical cell usually O₂ and H₂ can be produced and this is environmentally acceptable); *more friendly workplace* (*the cell house is for sure a more friendly workplace when compared to the pyrometallurgical plants*); *modularity* (the electrochemical plant is fully modular because its productivity is proportional to the number of cells) and *economics* (the plants don't require the big capacity of a thermal plant). However processes to recover lead from battery paste via electrowinning have several problems, one of which is the use of electrolyte solutions. Electrolytic lead recovery methods based on aqueous electrolytes including, for example, acetic acid, fluoboric acid, fluosilicic acid, alkanesulfonic acids etc., have been described [3]. Each of these acidic materials demonstrate certain problems which makes replacement thereof in electrolyte solutions at least desirable. For example, fluoboric acid cannot be discharged into many municipal waste-treatment systems due to restrictions of fluoride and boron discharges. The lead salt of acetic acid is highly soluble but acetic acid is weak electrolyte with poor conductivity at high concentrations leading to excessive power consumption. Fluosilicic acid is a toxic material which cannot be discharged to the environment.

This exploratory work examines the feasibility of electrowinning using the lead –complex system. In the study an organic amine was used as a chelating agent because of the stable lead-chelate compound and because of the prevalence with which this chelating agent is used to extract selectively base metals from hydroxide sludges which are produced in the treatment of acid mine drainage. Voltammetry measurements and electrodeposition were run to establish electrolysis conditions, lead deposit quality and ligand stability. The purpose of the study was to examine the effect of current density, additives, lead and ligand concentration on lead recovery efficiency.

Experimental

Solutions

All reagents used for the polarization measurements were of grade 98 – 99,9%. However lead compounds used in electrolysis experiments were obtained from waste battery paste using separating dissolution procedure.

The majority of the test solutions contained lead carbonate with concentration of lead (II) ions from 20 to 70 g/L, sulfuric acid (60 g/L) and an organic amine (150 – 200 g/L). The electrolysis tests were conducted with adding gelatine at concentration of 0.25, 0.50 and 1.00 %.

During the experiment, solution temperature was kept constant by a thermostat. As-prepared pH values of the test solutions vary insignificantly in the range from 9.90 to 10.25. Before and after each experiment pH

and conductivity of the electrolyte were measured with pHmeter Corning 445 and Conductivity meter Jenway 4310.

Electrochemical measurements [4]

Experiments were performed using a three-electrode setup. The working electrode was stainless steel mounted in epoxy. The exposed area of 1 mm^2 was polished with 1,200 to 2,000 emery papers, rinsed with deionized water and ethanol, then dried in cool air immediately prior to measurements. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum electrode was used as the counter electrode. All potentials were reported versus the SCE. Potentiodynamic polarization scans were obtained with proprietary software running on a personal computer connected to a digital potentiostat/galvanostat (Model PGS-HH6D, manufactured by the Institute of Chemistry - Vietnam National Center of Sciences and Technology).

Measurements were started after electrode immersion in the test solution for 30 min at the open-circuit. The scan rate was 1 mV/s for the linear and $10, 50$ and 100 mV/s for the cyclic voltammetry.

Electrolysis experiments

Electrolytic cell consisted of a 500-ml beaker with a magnetic bar (stirring speed of 150 rpm) to increase electrolyte circulation. Test cathodes include lead and stainless steel with the latter ultimately being chosen. The cathode of $36 \times 20 \times 1\text{ mm}$ dimensions was placed between two anodes of graphite with $60 \times 40 \times 5\text{ mm}$ dimensions. The ratio of solution volume versus cathode area was 12 ml/cm^2 .

Hull cell technique was run to find out the optimal current densities for lead electrodeposition. Cathode potential was recorded during electrolysis time of 4 hours.

Results and discussion

Potentiodynamic polarization in lead complex solutions

A comparative test was conducted in the blank solution which contained only indifferent electrolyte ($60\text{ g/L H}_2\text{SO}_4$) and chelating agent (170 g/L). The cathodic polarization behavior of stainless steel in the blank solution showed only one reduction peak at very high negative potential (about -1050 mV (SCE)), which apparently referred to water reduction.

With the presence of lead (II) cations in test solutions, two reduction peaks at -670 mV and -850 mV were observed. Cathodic curves showed a limiting current region from -750 to -820 mV . Results from a series of potentiodynamic polarization scans at increasing lead ion concentrations were plotted in Figure 1. The first cathodic current peak was related to reduction of simple lead ions and the second peak was corresponded to reduction of the lead - amine complex. With increasing lead concentration in electrolyte solutions the current density of both reduction peaks augmented.

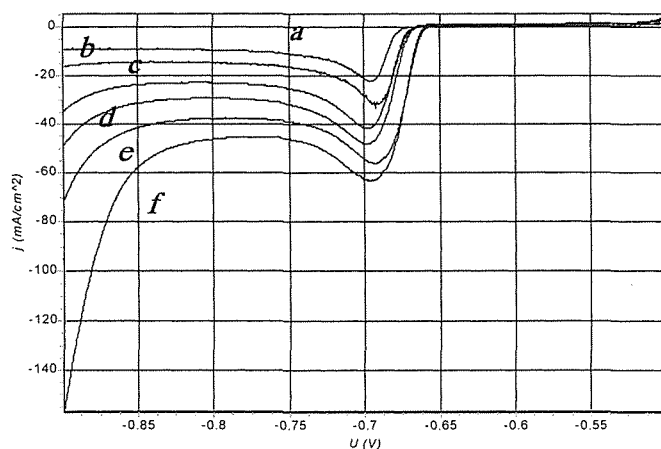


Figure 1: The linear polarization curves in solutions, containing $60\text{ g/L H}_2\text{SO}_4$, 170 g/L ligand and various lead ion concentrations: a - 20, b - 30, c - 40, d - 50, e - 60, f - 70 g/L

Influence of temperature on the cathodic current density of simple lead ion reduction is presented in Figure 2. At all studied temperatures from 30 to 60°C, reduction current density increased almost linearly with lead concentration in solution.

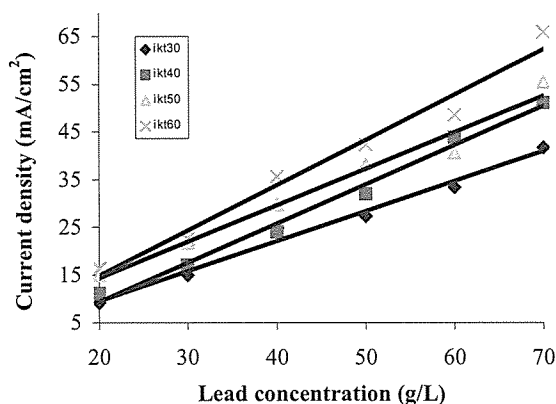


Figure 2: Current density at the reduction peak ($-0.700 \text{ V}_{\text{SCE}}$) versus lead concentration in solutions containing 60 g/L H_2SO_4 and 160 g/L chelating agent at various temperatures.

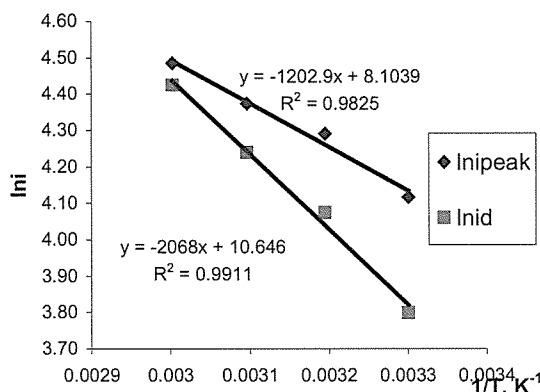


Figure 3: The relations of $\text{Log } i_{\text{peak}}$ (at -0.700 V -upper line) and $\text{Log } i_d$ ($-0.800 \text{ V}_{\text{SCE}}$) versus $1/T$ for lead reduction in the solution containing 70 g/L Pb^{2+} (PbCO_3), 60 g/L H_2SO_4 and 160 g/L chelating agent.

In Figure 3, the logarithms of current density values at the first peak potential (-700 mV) and at current plateau (-800 mV) were plotted versus inverse absolute temperature for calculating the activation energy of the lead electrodeposition reaction. The activation energy values calculated from the slopes of these linear relations were low, showing that the diffusion played a significant role in the lead reduction kinetics for the complex solutions, *i.e.* the electrodeposition of lead in these solutions was mass-transport limited.

An example of the cyclic voltammetric experiments for stainless steel in lead –complex solutions is shown in Figure 4.

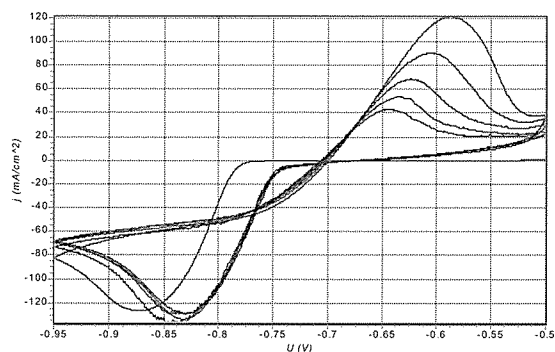


Figure 4: Cyclic voltammograms at 50mV/s on stainless steel in the solution of 70g/L Pb^{2+} , 175g/L amine, 70g/L H_2SO_4 at 30°C.

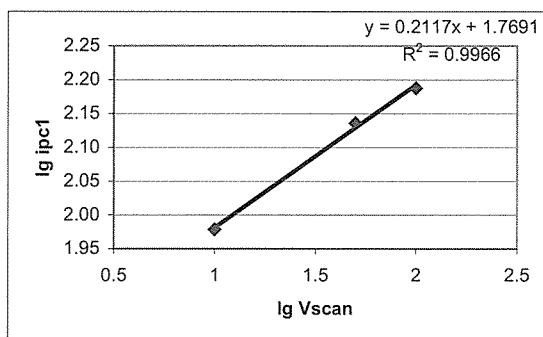


Figure 5: The logarithmic relation between cathodic current density peak of the first cycle and scan rate.

All cyclic voltammograms showed a 50 mV shift into positive direction of the reduction potential of lead ions and current peak potential from the second cycle in comparison with the first scan cycle. This was clearly due to the decrease of lead reduction overvoltage since after the first scan cycle there was a fine lead metal film formed on steel working electrode. The decrease of anodic current peak and the shift of this peak potentials into negative direction from scan to scan proved the passivity of lead oxidation in alkaline solutions [5].

These results showed that lead metal film formed on steel was not completely dissolved by oxidation reaction during the anodic scan.

Figure 5 presented logarithmic relation between cathodic current peak and scan rate.

The slope of the plot $\text{Log } i_{\text{peak}} = f(\text{Log } v_{\text{scan}})$ is about 0.2. Such low slope value proved again the role of diffusion [5] in the lead electrodeposition reaction for the studied complex solution.

From voltammetry results it was supposed that stainless steel could be used as the cathode for lead electrowinning and some electrolysis parameters, such as reduction potential, current density, etc., were found.

Electrolysis Tests

Effect of Additives

A problem of the electrolysis was dendrite metal deposit at the edges and corners of the electrode. To improve the quality of lead deposit, gelatin was added. With additive concentration increasing from 0.25 to 1% the deposit became more and more smooth and solid. However the solution became less transparent in excess of the additive. Ultimately the additive concentration of 0.5% was chosen for all electrolysis experiments.

Hull Cell Tests

Hull cell technique is an efficient tool to determine the optimal current densities for metal electrodeposition. The basic equation of Hull cell is

$$D_x = 10 \cdot I \cdot (a - b \cdot \lg x)$$

where x is the distance from nearest to furthest position of cathode, a and b are the cell constants. In the case of 267 ml Hull cell volume, a is 5.1 and b is 5.24.

In our tests, a Hull cell with volume of 267ml was used and applied direct current changed from 1 to 5 A. The test results showed an optimal range of the cathodic current density should be between 7.5 - 20mA/cm² when the current of 1A was applied to the cell. So the current density values from 5 to 30mA/cm² were chosen for studying its effect on lead electrodeposition process.

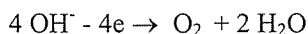
Effect of Current Density

Some parameters for lead deposition on stainless steel cathode in 4 -hour electrolysis of the solution containing 60 g/l H₂SO₄; 70 g/l Pb²⁺ (PbCO₃) and 160 g/l chelating agent (solution A) are presented in the Table 2.

The cathode potential was stable during the electrolysis. Also the electrolyte pH was nearly unchanged, while the solution conductivity increased slightly. Bubbles were seen to form on the anode, presumably it was oxygen gas.

It was obviously that in studied conditions there was only the reduction of lead ions. Obtained product was analysed by XRD and XRF spectroscopy, showing the lead purity of 99,97%. Solution analysis before and after electrolysis also proved that the ligand was not decomposed during electrolysis, which was in accordance with the results in [6].

Thus, the reaction at the anode was the oxidation of water. In the basic media oxygen was liberated by the following reaction:



and the consumption of OH⁻ was the reason of slight fall of pH.

Table 2: Influence of current density on the electrolysis parameters for the solution A
(m_{Pb}: lead deposit mass on 1 cm² – cathode area.)

i, mA/cm ²	m _{Pb} , g/cm ²	Current efficiency, %	E _{cathode} , V	pH	κ, mS
5,0	0,0772	99,87	0,681	10,01	25,90
7,5	0,1115	96,17	0,679	9,99	26,30
10,0	0,1524	98,64	0,678	9,99	26,40
12,5	0,1916	99,15	0,682	9,99	26,73
15,0	0,2292	98,90	0,684	9,98	27,13
17,5	0,2650	97,92	0,679	9,95	27,50
20,0	0,2981	96,39	0,681	9,95	27,30
30,0	0,4597	99,49	0,702	9,92	25,63

Figure 6 showed the linear relationship between of lead deposited mass on 1cm² of cathode area and current density. In all the studied range of current density (from 5.0 to 30.0 mA/cm²), current efficiency of lead deposition was over 96%.

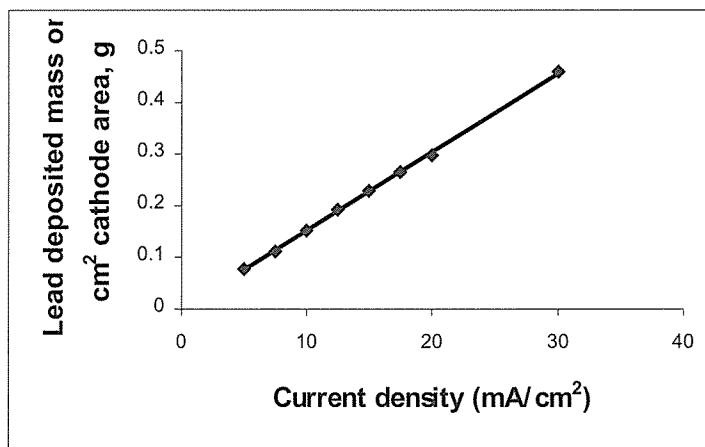
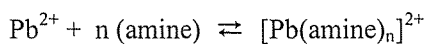


Figure 6: Deposited lead mass after 4-hour electrolysis of solution A as a function of current density

Effect of ligand concentration

Electrolysis at low current density showed a decreasing of lead deposit mass increasing ligand concentration in the solution. Figure 7 showed an inverse proportion of lead deposit mass on 1 cm² cathode area to ligand concentration during 4-hour electrolysis at 10 mA/cm² in the solution containing 60 g/l H₂SO₄; 70 g/l Pb²⁺ (PbCO₃) with chelating amine content augmented from 150 to 200 g/L

It was supposed that at low current density the reduction occurred on the cathode was of free lead cations but not of complex ions. In addition, the ligand chosen was not very strong chelating agent and there is a complex forming equilibrium in the electrolyte solution:



The increase of ligand concentration in the solution shifted this equilibrium into formation of complex ions and in consequence of this, the concentration of free lead (II) ions in the solution was diminished, leading to decrease of deposit mass. Besides, the viscosity of ligand concentrated solutions increased as well, which might impede the movement of free lead (II) cations to the cathode.

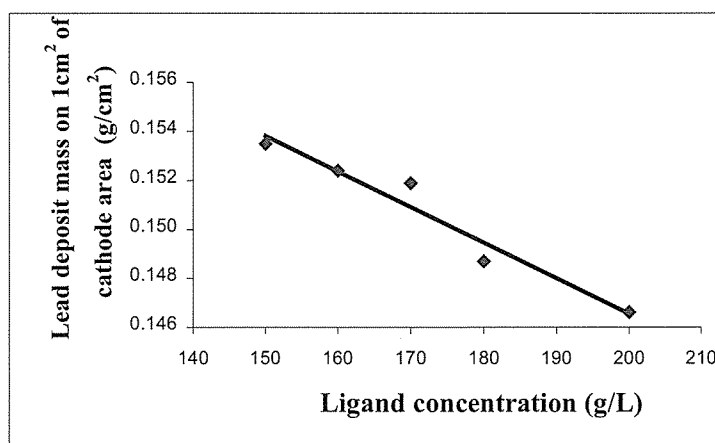


Figure 7: Lead deposited mass as a function of ligand concentration (60 g/L H₂SO₄, 70 g/L Pb²⁺, ic = 10 mA/cm², 4-hour electrolysis)

Conclusions

Results of this showed that the studied amine could be used as a chelating agent in alternative electrolyte solutions for lead recovery from waste battery paste by electrodeposition.

Lead electrodeposition process and the quality of obtained lead metal were studied using linear and cyclic voltametry as well as by a bench-scale electrolysis. The optimal values were found for electrolysis parameters, such as: current density ($20 - 30 \text{ mA/cm}^2$), cathode potential ($650 - 700 \text{ mV/SCE}$) and ligand concentration ($160 - 170 \text{ g/L}$). Stainless steel showed to be an excellent material for the cathode, while graphite was a good anode; in all electrolysis experiments lead dioxide (PbO_2) was not formed at the anode, which was an advantage of the studied solutions.

In this study, the chelating agent solutions were regenerated once; however it is unknown whether there is a limit to regeneration that will produce unusable chelating agent solution. Multiple regeneration of the ligand solution should be investigated to determine the extent of regeneration of the chelating agent.

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