Journal of Hazardous Materials 217–218 (2012) 452–456

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Short communication

Improved lead recovery and sulphate removal from used lead acid battery through Electrokinetic technique

C. Soundarrajan, A. Sivasankar, S. Maruthamuthu*, A. Veluchamy

CSIR-Central Electrochemical Research Institute, Karaikudi 630 006, India

ARTICLE INFO

Article history:
Received 11 November 2011
Received in revised form 23 February 2012
Accepted 13 March 2012
Available online 23 March 2012

Keywords:
Electrokinetics
Agar membrane
Nafion
ULAB

ABSTRACT

This paper presents improvement in lead (Pb) recovery and sulphate removal from used Pb acid battery (ULAB) through Electrokinetic technique, a process aimed to eliminate environmental pollution that arises due to emission of gases and metal particles from the existing high temperature pyrometallurgical process. Two different cell configurations, (1) one with Nafion membrane placed between anode and middle compartments and Agar membrane between cathode and middle compartments and (2) another with only Agar membrane placed between both sides of the middle compartments were designed for the Pb and sulphate separation from ULAB. This paper concludes that the cell with only Agar membranes performed better than the cell with Nafion and Agar membranes in combinations and also explains the mechanism underlying the chemical and electrochemical processes in the cell.

1. Introduction

Following the invention of lead (Pb) acid battery by Gaston Planté, its application to automotive and domestic sector has increased by several folds. This resulted in the accumulation of spent batteries which became the source for soil and air pollution. Now, it is well known for its toxicity toward nerve, kidney and reproductive systems and also for its threat to living organism in land and under-sea even in trace quantity of Pb [1,2].

The cost effective Pyrometallurgical route was in vogue for several decades for the Pb and sulphate recovery. As this process had emission of Pb and sulphur compounds into environment [3], less pollutant processes such as Hydrometallurgical and Electrowinning technique [4] were developed, but these also needed replacement as they employed hazardous HBF_4 as electrolyte [4–8].

Literature survey shows that Electrokinetics is an emerging technique finds a place for the removal of polluting materials such as the heavy metal pollutants from sewages and industrial wastes [9–13]. In our previous paper [14] we described the application of electrokinetics for the separation of Pb and sulphate in acetic acid medium. This paper describes the application of the same tool for the separation of Pb and sulphate in ammonium acetate in two different cell designs and explains the results based on reaction mechanism.

2. Materials and methods

2.1. Sample material

The sample material for the electrokinetic experiment was obtained in the form of fine powder by crushing the ULAB in a crusher and then separating the Pb metal from the oxides and sulphates of Pb. Small amount of carbon and lignin present in the powder material was separated by adopting floatation method. This allows light weight carbon and lignin to be carried away by the running water and Pb compounds to get settled down. The water in the beaker was decanted and the remaining powder was dried in the air oven. The fine powder obtained was used for the experiment.

2.2. Separators

Two cells with different designs named as Cell-A and Cell-B were used for the present investigation. Cell-A incorporated Nafion separator between the anode and middle compartments and Agar separator between cathode and middle compartments. For comparison another cell (Cell-B) was constructed with Agar membrane as separators placed on both compartments of the cell (Fig. 1). The agar solution for the membrane preparation was made by simply dissolving 2 g of agar in 100 ml distilled water in a beaker under stirring condition over a hot plate. It was then poured onto the pores of acrylic sheets (thickness 1 mm) and cooled to obtain gel filled perforated acrylic separator (GFPA-separator).

---

* Corresponding authors. Tel.: +91 4565 227550; fax: +91 4565 227779.
E-mail addresses: biocorrcecri@gmail.com (S. Maruthamuthu), Veluchamy.a@gmail.com (A. Veluchamy).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2012.03.040

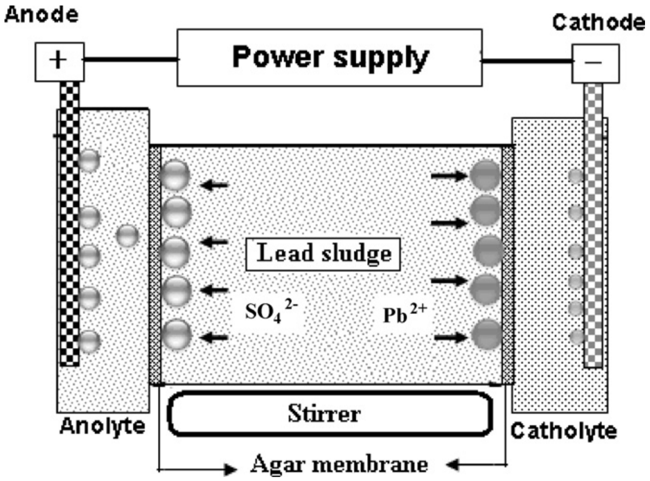

Fig. 1. Typical Electrokinetic (EK) cell with Agar membrane separator.

2.3. Cell set up

The schematic diagram of Electrokinetic (EK) cell which consisted of a middle compartment separated by two adjacent compartments, one for the cathode and another for the anode was made out of acrylic sheets of dimensions $24 \times 4 \times 6\,cm^3$ (Fig. 1). The cell was placed over an electromagnetic stirrer to maintain uniform distribution of the sample solution in the central compartment during EK experiment.

2.4. Electrolyte

The middle compartment was filled with 10 g of the sample material along with 100 ml of 0.3 M ammonium acetate and maintained at pH < 3 during experiment by adding appropriate quantity of nitric acid [15]. The visual observation indicates that the Pb-compounds in the middle compartment are sparingly soluble in the electrolyte. However, during EK experiment the concentration gradient caused by the depletion of small/available amount of Pb ions in the cathode compartment remained as driving force for the release of Pb^{2+} ions from the sparingly soluble Pb-compounds present in the middle compartment. 0.3 M acetic acid was used as anolyte and its pH was kept at ∼3 using glacial acetic acid at the beginning of the experiment. The catholyte solution is 0.1 M KNO_3, the pH was maintained between 4 and 5 using glacial acetic acid [14].

2.5. Electrodes

In both cells, the TSIA (titanium substrate insoluble anode) and Ti (titanium) were used as anode and cathode respectively. The area of the electrode was kept the same as in our previous paper [14].

2.6. Instrumentation

The DC power required for the EK cell was provided by Aplab power supply model: regulated power supply L 3205 with a variable voltage from 0 to 32 V. The pH of the anolyte and catholyte was measured during EK operation by using the pH meter model "EUTECH instrument PH510 cyber scan". The XRD pattern of the lead acid battery scrap were recorded using computer controlled XRD system, JEOL, and Model:JPX 8030 with CuKα radiation (Ni filtered = 13,418 Å) at 40 kV and 20 A current. The peak search and peak match program built with software (syn master 7935) was used to identify the compounds. The purity of lead after EK was analysed by employing thermal analyser (TGA). Thermal analyser model: TA Instruments Model SDT Q600 and heating rate of 20 °C/min in air atmosphere.

3. Results and discussion

In our previous paper, we reported that the oxygen diffuses into the middle compartment from the anode compartment and reacts with the lower valent Pb oxides and free Pb^{2+} ions present in the middle compartment, thus making the middle compartment rich with large amount of insoluble Pb oxides, especially in the cell where TSIA anode was used.

In this paper, hence an attempt was made to prevent the oxygen diffusion by using Nafion separator which permits only H^+ to diffuse and not the oxygen. We also hoped that diffusion of H^+ into the middle compartment could facilitate $PbSO_4$ dissociation. Such dissociation reaction is expected to increase the acidity in the middle compartment due to accumulation of H_2SO_4 and also favour deposition of higher amount of Pb in the cathode compartment.

This expectation lead to construct a cell (Cell-A) containing Nafion separator between the anode compartment and middle compartment. For comparison, another cell (Cell-B) was constructed with Agar membrane as separator between middle and adjacent compartments. From the X-ray (Fig. 2), it becomes clear that the prominent sparingly soluble compounds in the sludge are $PbSO_4$, $Pb(S_2O_3)$ and PbO. As we have $NH_4(CH_3COO)$ in the middle compartment, the possible reactions are

$$PbSO_4 + 2NH_4(CH_3COO) \rightleftharpoons Pb(CH_3COO)_2 + (NH_4)_2SO_4 \quad (1)$$

$$Pb(S_2O_3) + 2NH_4(CH_3COO) \rightleftharpoons Pb(CH_3COO)_2 + (NH_4)_2S_2O_3 \quad (2)$$

$$PbO + 2NH_4(CH_3COO) + 2H^+ \rightleftharpoons Pb(CH_3COO)_2 + 2NH_4OH \quad (3)$$

The $Pb(CH_3COO)_2$, even though a weak salt, could undergo easy dissociation in the presence of nitric acid present in the central compartment as,

$$Pb(CH_3COO)_2 + 2H^+ \rightarrow Pb^{2+} + 2CH_3COOH \quad (4)$$

The Pb^{2+} ions could diffuse into cathode to undergo reduction as Pb and equivalent amount of $SO_4{}^{2-}$ and $S_2O_3{}^{2-}$ diffuses to anode compartment for charge compensation. The compounds $(NH_4)_2SO_4$ and $(NH_4)_2S_2O_3$ are highly ionizable.

$$(NH_4)_2SO_4 \rightarrow 2NH_4{}^+ + SO_4{}^{2-} \quad (5)$$

$$(NH_4)_2S_2O_3 \rightarrow 2NH_4{}^+ + S_2O_3{}^{2-} \quad (6)$$

$S_2O_3{}^{2-}$ diffuses to anode, oxidizes there as $SO_4{}^{2-}$ which may be represented by the following reactions

$$S_2O_3{}^{2-} + 2O_2 \rightarrow SO_4{}^{2-} + SO_3{}^{2-} \quad (7)$$

$$SO_3{}^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4{}^{2-} \quad (8)$$

However, it was observed only low amount of Pb got deposited in the cathode compartment. If the H^+ diffused into the middle compartment the expected dissociation reaction is, $PbSO_4 + H^+ \rightarrow Pb^{2+} + H_2SO_4$, which must facilitate Pb deposition in the cathode, provided, for charge compensation equal amount of negative ions such as $SO_4{}^{2-}$, $S_2O_3{}^{2-}$ and O^{2-} diffuse into the anode. However, the low Pb deposition indicates that the anionic movements from central compartment to anode compartment could not occur as Nafion separator is only proton conducting one.

The Cell-B constructed by using Agar membrane, a polymer with subunits of sugar galactose, performed better and yielded higher Pb deposition at the cathode. The porous membrane facilitated easy diffusion of both anions and cations, ultimately to better separation of sulphates and Pb in the cell compared to that in the Cell-A.

The procedures described earlier [14] were followed to estimate the quantity of free sulphate present in the anode and middle compartments through gravimetric estimation. The Pb collected in the