



Short communication

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

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## 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.

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### 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  $\text{HBF}_4$  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 (GPPA-separator).

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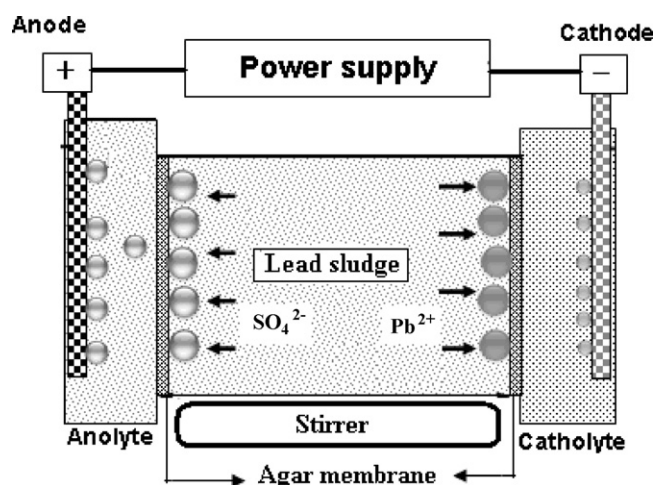


Fig. 1. Typical Electrokinetic (EK) cell with Agar membrane separator.

### 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  $24 \times 4 \times 6 \text{ cm}^3$  (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  $\text{pH} < 3$  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  $\text{Pb}^{2+}$  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  $\sim 3$  using glacial acetic acid at the beginning of the experiment. The catholyte solution is 0.1 M  $\text{KNO}_3$ , 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  $\text{CuK}\alpha$  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

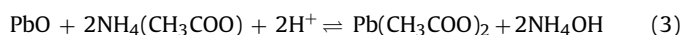
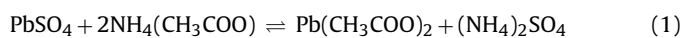
analyser model: TA Instruments Model SDT Q600 and heating rate of  $20^\circ\text{C}/\text{min}$  in air atmosphere.

## 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  $\text{Pb}^{2+}$  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  $\text{H}^+$  to diffuse and not the oxygen. We also hoped that diffusion of  $\text{H}^+$  into the middle compartment could facilitate  $\text{PbSO}_4$  dissociation. Such dissociation reaction is expected to increase the acidity in the middle compartment due to accumulation of  $\text{H}_2\text{SO}_4$  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  $\text{PbSO}_4$ ,  $\text{Pb}(\text{S}_2\text{O}_3)$  and  $\text{PbO}$ . As we have  $\text{NH}_4(\text{CH}_3\text{COO})$  in the middle compartment, the possible reactions are



The  $\text{Pb}(\text{CH}_3\text{COO})_2$ , even though a weak salt, could undergo easy dissociation in the presence of nitric acid present in the central compartment as,



The  $\text{Pb}^{2+}$  ions could diffuse into cathode to undergo reduction as Pb and equivalent amount of  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  diffuses to anode compartment for charge compensation. The compounds  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  are highly ionizable.



$\text{S}_2\text{O}_3^{2-}$  diffuses to anode, oxidizes there as  $\text{SO}_4^{2-}$  which may be represented by the following reactions



However, it was observed only low amount of Pb got deposited in the cathode compartment. If the  $\text{H}^+$  diffused into the middle compartment the expected dissociation reaction is,  $\text{PbSO}_4 + \text{H}^+ \rightarrow \text{Pb}^{2+} + \text{H}_2\text{SO}_4$ , which must facilitate Pb deposition in the cathode, provided, for charge compensation equal amount of negative ions such as  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{O}^{2-}$  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

**Table 1**

The table compares accumulated sulphates in the anolyte and middle chamber and also the Pb recovered in the cathode compartments for the Cell-A and Cell-B.

Cell	No. of days	Sulphates		Recovered Pb at cathode (g)
		In 200 ml of anolyte (mg)	In the middle compartment (mg/g)	
Cell-A	12	Nil	~121.2	~5.21
Cell-B	2	~46.1	~83.8	~7.20

cathode compartment was weighed and presented in Table 1 and it shows that the cell with all Agar-separator membrane performs better than the cell with Nafion-Agar membrane separators.

Even though the amount of sulphate in lead acid battery scrap is ~141 mg/g (estimated through quantitative analysis), the anolyte of the Cell-A does not contain even a trace of sulphate after EK experiment, but the Cell-B showed the sulphate content as ~46.1 mg implying that Nafion does not allow movement of sulphate into the anolyte due to its specific preference only toward  $H^+$  diffusion. In our previous paper [14] we reported that the quantity of sulphate removed from the sludge in 30 days was about 43% in the EK process that uses filter paper as membrane. This paper describes that even in a period of about 2 days it became possible to recover 32.6% of sulphate. Fig. 2 depicts the X-ray diffraction spectrums of the scrap which shows the most prominent peaks are due to the compounds  $PbSO_4$ ,  $Pb_3O_2$ ,  $SO_4$  and  $PbS_2O_3$ . The other peaks due to compounds and elements are  $PbO_4Pb(SO_4)$ ,  $Pb_3O_4$ ,  $Pb_2O_3$ ,  $PbS$  and  $Pb$ . As  $Pb$  forms oxides that are non-stoichiometric, formation of several sub-oxides and basic sulphates could be expected to form during overcharging of the battery plate.

Fig. 3 shows how the pH is maintained in the Cell-B during the EK experiment. Acidic pH at the cathode is required in order to favour electrodeposition of  $Pb$  ions as well as to neutralize the hydroxyl ions formed at the cathode. Even though the pH at the beginning of the experiment is kept between 2 and 3, the pH tends to become more acidic due to the release of more amount of  $H^+$  from the anode.

Fig. 4 shows the amount of  $Pb$  deposited with time in the cathode of Cell-B. The curve shows that during the early period of EK experiment, higher quantity of  $Pb$  deposits and as the time passes  $Pb$  deposition decreases which indicate the non-availability of sparingly soluble  $Pb$  compounds (the source for  $Pb^{2+}$  ions) for electrodeposition.

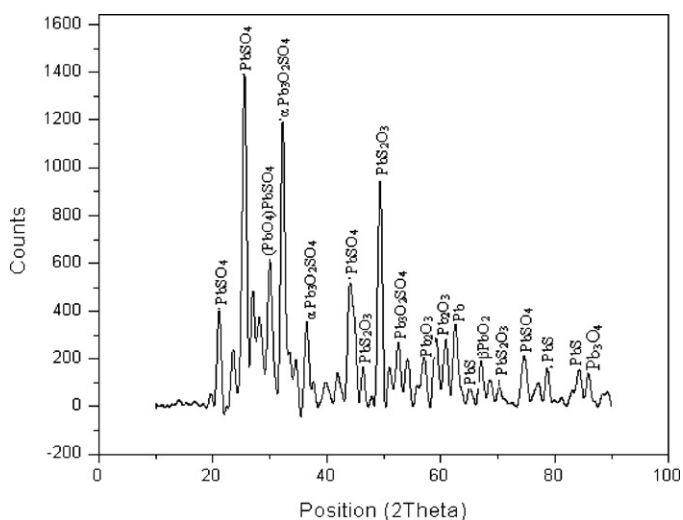


Fig. 2. X-ray spectrum depicting various chemical species present in the Pb acid battery scrap.

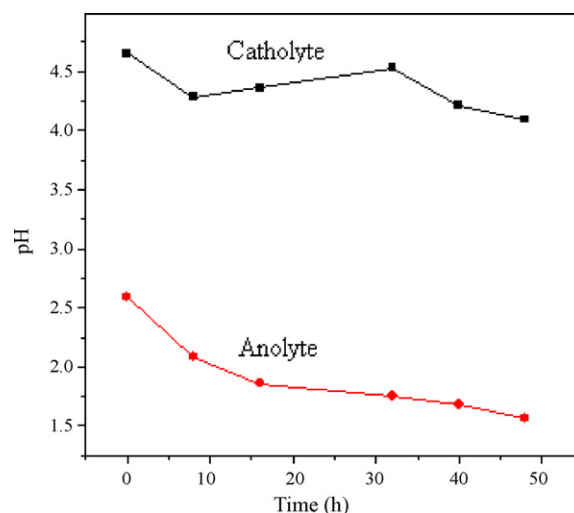


Fig. 3. Variation of pH with time (h) for the anolyte and catholyte of Cell-B.

Thermogravimetric analysis was carried out for the cathodically deposited  $Pb$  in the Cell-B (Fig. 5). The experiment is carried out in air which permits easy decomposition of organic impurities. The curve shows slow decrease of sample weight with temperature up to  $300^\circ C$ . During the early part of the curve the weight decrease is attributed to evaporation of water molecules and later part is due to oxidizable organic impurities. The organic impurities may be expected to react with lead oxides/sulphates present in the sample and leave as gases such as  $CO_2$  and  $SO_2$ . This early weight loss comes to about 8.14% which is due to removal of water and organic impurities. The recovered purity of  $Pb$  is about 91.42%. This purity was found to be more when compared to TSIA-EK system (86%) [14]. The inflection point at  $333.22^\circ C$  in the DTA curve is attributed to melting point of  $Pb$ .

In our previous paper, the  $Pb$  sludge was packed in the central compartment where filter paper was used to avoid the movement of sludge particles from the central compartment into anodic or cathodic compartments. While using TSIA, the efficiency became less compared to that in  $Ti$  electrode system. It was explained that high oxygen evolution from TSIA created oxidizing environment, converted most of  $Pb$  compounds into  $Pb$  oxides/basic oxides lead to the formation of insoluble  $Pb$  compounds. The study also revealed

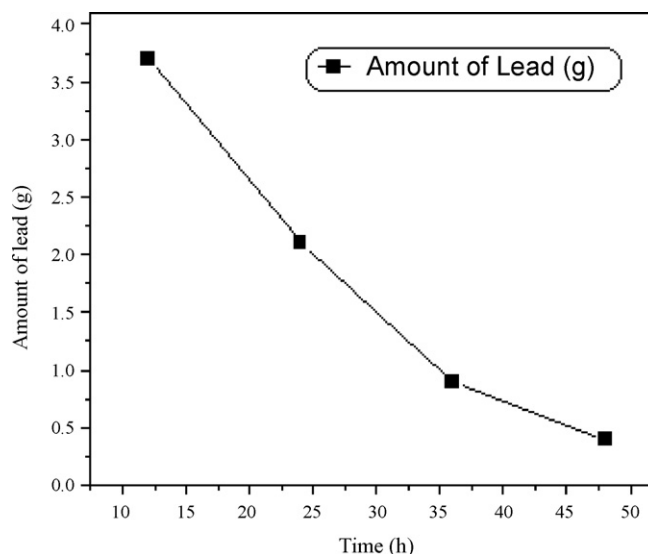


Fig. 4. Amount of lead recovered with time (h) at the cathode of Cell-B.

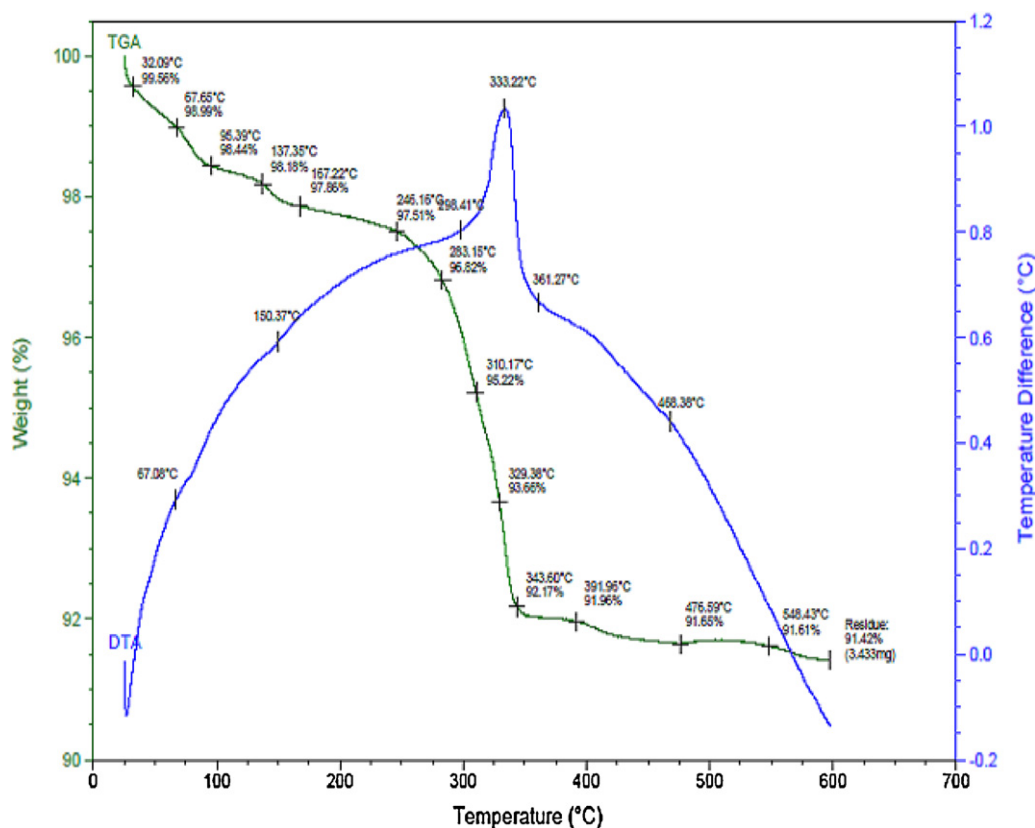


Fig. 5. TGA spectrum of the lead recovered at the cathode of Cell-B.

application of voltage causes migration of more sulphate ions from the central compartment to the anode side in the Ti-EK cell than that in TSIA-EK cell [14].

In the present study, we showed ammonium acetate electrolyte with Agar membrane has resulted in higher Pb recovery compared to the cell with Nafion membrane. In the Cell-B with Agar membrane the Pb recovery was 7.20 g (72%) in 2 days. In the previous study [14], 21% and 23% of Pb was recovered in 30 days by employing TSIA and Ti electrodes respectively. Sulphate removal was also higher by ~32.6% in 2 days when compared to previous study.

#### 4. Conclusion

In our previous paper, it was reported that the diffusion of oxygen into central compartment from the anode compartment caused formation of large amount of lead oxides in the middle compartment. In the present report, the EK experiments were designed to prevent the diffusion of oxygen from the anode compartment into central compartment by incorporating Nafion membrane between the anode compartment and middle compartment. This membrane permits  $H^+$  into the middle compartment which results in higher acidity in the middle compartment with time. Such increase in acidity is expected to favour dissociation of  $PbSO_4$  and consequently higher Pb deposition at the cathode. But actually we obtained very low deposition of Pb. This shows that increase of acidity alone is not sufficient to drive the  $Pb^{2+}$  ions into the cathode compartment but also requires equivalent quantity of sulphate ion diffusion into the anode compartment for charge compensation. While in the cell employing Agar membrane, the sulphate and  $Pb^{2+}$  ions diffuses into the anode and cathode compartment respectively resulting in efficient Pb recovery which is further improved by agitating the solution using a stirrer. The solution in the middle compartment

when agitated diminishes the concentration gradient, results in efficient Pb deposition.

The Nafion separator deters the sulphate ions transport whereas the Agar membrane favours easy sulphate ion transport into the anodic compartment. Sulphate ion movement into anode favours Pb ions to diffuse into the cathodic region, a prerequisite for charge compensation. Hence the configuration employed in Cell-B is more preferred over the Cell-A with Nafion separator for Pb recovery and sulphate separation.

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