

B. Rezaei · S. Damiri

Application of surface electrochemical passivation of lead-antimony alloy for a simple and rapid electrochemical determination of antimony content

Received: 31 March 2005 / Revised: 27 April 2005 / Accepted: 2 May 2005 / Published online: 26 July 2005
© Springer-Verlag 2005

Abstract A simple, rapid and selective electrochemical method is proposed as a novel and powerful analytical technique for the solid phase determination of less than 4% antimony in lead-antimony alloys without any separation and chemical pretreatment. The proposed method is based on the surface antimony oxidation of Pb/Sb alloy to Sb(III) at the thin oxide layer of PbSO₄/PbO that is formed by oxidation of Pb and using linear sweep voltammetric (LSV) technique. Determination was carried out in concentrate H₂SO₄ solution. The influence of reagent concentration and variable parameters was studied. Antimony of Pb/Sb alloys can be determined in the range of 0.0056–4.00% with a detection limit of 0.0045% and maximum relative standard deviation of 4.26%. This method was applied for the determination of Sb in lead/acid battery grids satisfactory.

Keywords Lead alloy · Antimony · Linear sweep voltammetry

Introduction

Antimony is widely used for production different types of lead alloy for different applications. One of the most frequent applications of lead-antimony alloys is for grids production of lead-acid battery. Antimony improves the castability and the subsequent handling of the grid alloy. In addition, these alloys are extremely strong and creep-resistant and can be cast into rigid, dimensionally stable grids that are capable of resisting the stresses of charge/discharge reactions [1–2]. The use of low-antimony alloys is an effective means to minimize

gassing and to achieve maintenance-free lead-acid batteries, thus during the 30 last years the electrochemical behavior of this alloys has been the research subject of many investigators [3–9].

On the other hand, these alloys are extensively used as suitable electrode in electroplating and electrowinning plants. antimony concentration is very effective on the quality of Pb/Sb alloy applications, hence simple, rapid and selective determination of Sb is very important.

Several classical and instrumental analytical techniques have been reported for the determination of antimony in lead alloys such as polarography[10], potentiometry [11], spectrophotometry [12], neutron activation analysis [13, 14], radioisotopic X-ray analysis [15] and atomic absorption spectroscopy (AAS) [16, 17]. Most of proposed methods that are used for determination of antimony in lead alloys may be sensitive, but some of them are time consuming or needs various reagents for the chemical pretreatment and separation of lead or tin for eliminating interfering effect. Therefore cost of analysis is high and samples rate analysis is very low. However by using of Quantometric method, samples rate analysis is increased, but the apparatus is more expensive.

In this work, by using electrochemical behavior of lead-antimony alloys that has been extensively studied during the last years for improving the lead-acid battery performance, a useful and very fast method based on passivation of this alloy in sulfuric acid, has been developed for the determination of Sb in low antimony (less than 4%) Pb–Sb alloys.

Experimental

Apparatus and reagents

The iron mould with cooling system and temperature control unit was used for preparing of working electrode. The working electrode was a wire with cross section area of 0.5 cm² that is made of lead-antimony

B. Rezaei (✉) · S. Damiri
College of Chemistry, Isfahan University of Technology,
Isfahan, 84156 Iran
E-mail: rezaei@cc.iut.ac.ir
Tel.: +98-31-13912351
Fax: +98-31-13912350

alloys and it's around is mounted with an epoxy resin. Before the experiment, the electrode was mechanically polished with water-resistant emery paper and washed with acetone. The sulfuric acid solution with various molar concentrations was used as the electrolyte. The voltammograms were obtained at sweep rate 200 mV s^{-1} , in the potential range -0.7 V to $+0.7 \text{ V}$, using potentiogalvanostat of Behpajoooh Co. Model BHP-2061-C. A model LAVFC03A multichannel Quantometer(Spectrolab) and its various Pb/Sb standards with ref. number: R Pb 11–15 were used to measuring antimony of lead alloys as a standard method. The experiments were carried out at room temperature (298 K). The counter and reference electrodes were a platinum plate with 1 cm^2 of geometric area and $\text{Hg}/\text{Hg}_2\text{SO}_4$ respectively. All the chemicals used were of analytical reagents grade. A doubly distilled water was used for preparation of solution.

Recommended procedure

10 mL supporting electrolyte solution containing sulfuric acid 4.0 mol L^{-1} was pipette into the cell and the solution. A linear sweep voltammograms for pure lead working electrode was recorded from $+0.70$ to -0.70 V , with a potential scan rate of 200 mV s^{-1} . This current is named as I_{pb} . After the background voltammograms has been obtained, standard lead alloys with various antimony contents (0.0056 – 4.00%) were immersed into the cell and the above procedure was repeated to obtain sample peak current. This current is named as I_{ps} . All data were obtained at room temperature. Calibration graph were obtained by plotting the net peak current ($\Delta I_{\text{p}} = I_{\text{ps}} - I_{\text{pb}}$) against antimony concentration.

Results and discussion

The electrochemical behavior of Pb–Sb alloys electrodes and redox reactions that are occurring in acidic solutions are complex and depend on many variables, such as kinds and concentration of electrolytes and sweep rate. the electrochemical behavior of these alloys has been the research subject of many investigators [3–9]. The linear sweep voltammograms for the blank and sample electrodes in sulfuric acid solutions was shown in Fig. 1. As can be seen in this figure, for the pure lead electrode(blank) in a solution containing sulfuric acid, no obvious current peaks were observable between 0.0 to $+0.4 \text{ V}$. On the other hand, with the using of Pb/Sb electrodes (lead alloys contain various concentration of antimony), an anodic peak can be seen located at about $+0.1 \text{ V}$ versus Hg/HgSO_4 electrode. The anodic current increases with increasing of antimony content of lead–antimony alloys. The surface passivation of lead alloy with formation of PbSO_4/PbO cause that the peak of antimony in this potential region is observed by oxidation of antimony only as Sb(III) [7–9].

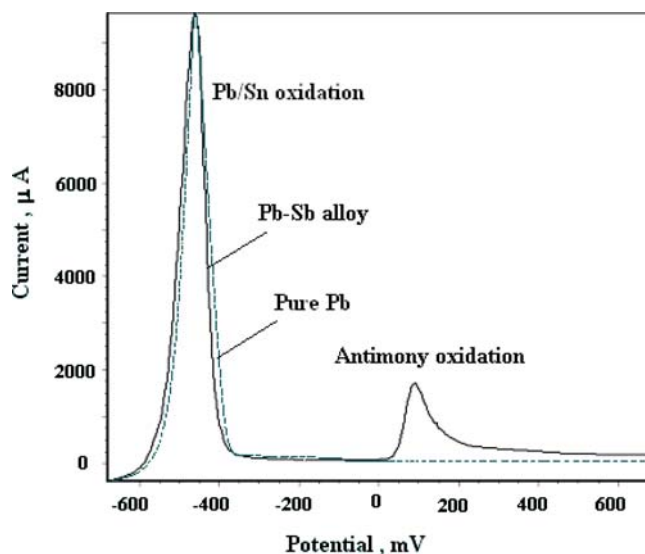


Fig. 1 Linear sweep voltammograms for Pb–Sb–Sn alloy (Sb wt. 1.66%; Sn wt. 0.24%) and a blank Pb alloy (99.998%); Conditions: sulfuric acid concentration, 4.0 mol L^{-1} ; initial potential, -0.70 V ; final potential, $+0.70 \text{ V}$; Scan rate, 50 mV s^{-1}

Influence of variables

To optimize condition, the effect of experimental parameters such as kinds and concentration of electrolyte, potential range (suitable initial potential for surface passivation and resolution between peak current of oxidation lead to PbSO_4/PbO and peak current due to oxidation of antimony to Sb(III)) and scan rate in linear sweep voltammetric determination of antimony were studied at room temperature with Pb–Sb–Sn (Sb wt. 1.66%; Sn wt. 0.24%). Preliminary experiments were carried out with different types of electrolyte such as perchloric, phosphoric and sulfuric acid. The results shown that the peak current and resolution between peak current of oxidation lead to PbSO_4/PbO and peak current due to oxidation of antimony to Sb(III) was improved in the presence of sulfuric acid (Fig. 2). Thus sulfuric acid solution was selected as the electrolyte.

The effect of sulfuric acid concentration was studied for the range of 1.0 – 9.0 mol L^{-1} (Fig. 3). The results shown that by increasing concentration of sulfuric acid peak current increases up to 4.0 mol L^{-1} , whereas greater sulfuric acid concentration decreasing the peak current. Thus a sulfuric acid concentration of 4.0 mol L^{-1} was selected.

Figure 4 shows the effect of variation of initial sweeping potential for surface passivation and resolution between peak current due to oxidation of lead and antimony at the optimum sulfuric acid concentration 4.0 mol L^{-1} . As expected, by decreasing the initial sweeping potential down to -0.70 V , the peak current of anodic oxidation of antimony and resolution between above peaks current increased. In the potential lower than -0.70 V , hydrogen gas evolution is carried out that

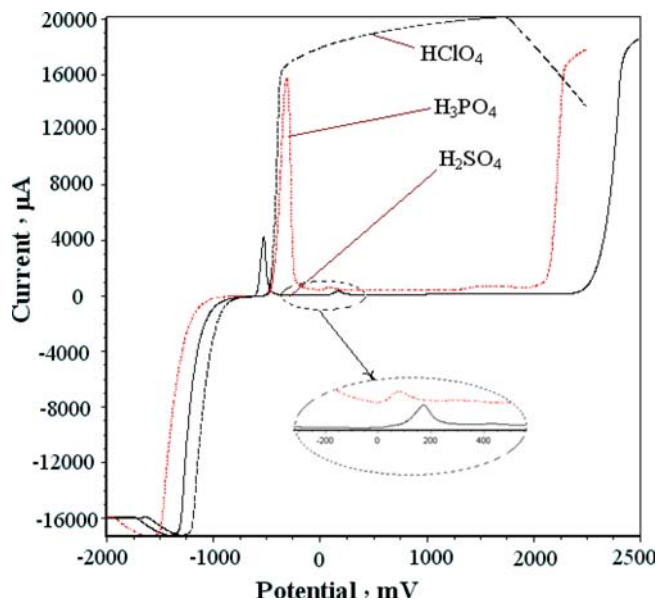


Fig. 2 Influence of types of electrolyte(perchloric, phosphoric and sulfuric acid) on the peak current and linear sweep voltammograms of Pb–Sb alloy. Conditions: Pb–Sb–Sn alloy(Sb wt. 1.66%; Sn wt. 0.24%); acid concentration, 4.0 mol L⁻¹; initial potential, -2 V; final potential, +2.5 V; Scan rate, 50 mV s⁻¹

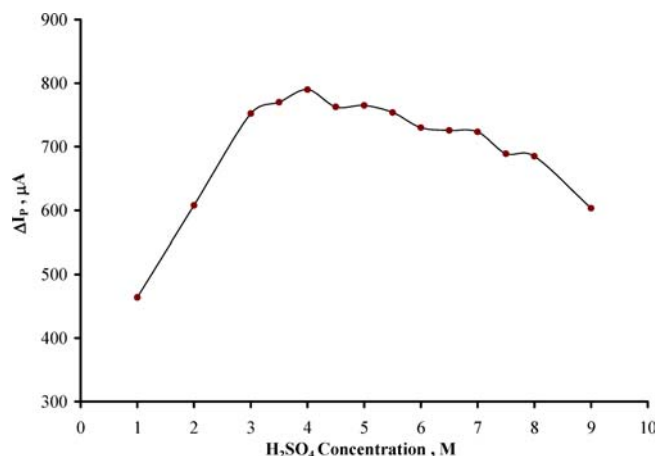


Fig. 3 Influence of sulfuric acid concentration on the sensitivity. Conditions: Pb–Sb–Sn alloy (Sb wt. 1.66%; Sn wt. 0.24%); initial potential, -0.70 V; final potential, +0.70 V; Scan rate, 50 mV s⁻¹

interferes on the determination. Thus -0.70 V was selected as an initial sweeping potential.

The influence of scan rate on the peak current of the anodic oxidation of antimony was examined over the range of 50–600 mV s⁻¹ for two alloys contain 1.66 and 2.72% on antimony (Fig. 5). The results shown that the peak currents increases up to 200 mV s⁻¹, with a linear relation between peak currents(ΔI_p) and a square-root of scan rate($v^{1/2}$). Thus scan rate of 200 mV s⁻¹ was selected for the study.

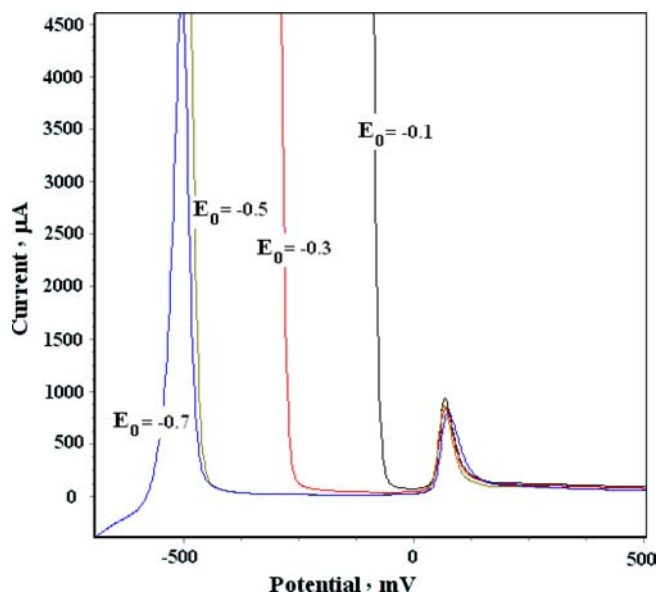


Fig. 4 Influence of initial sweeping potential on the resolution and peak current. Conditions: Pb–Sb–Sn alloy (Sb wt. 1.66%; Sn wt. 0.24%); sulfuric acid concentration, 4.0 mol L⁻¹; initial potential, -0.70 V; final potential, +0.70 V; Scan rate, 50 mV s⁻¹

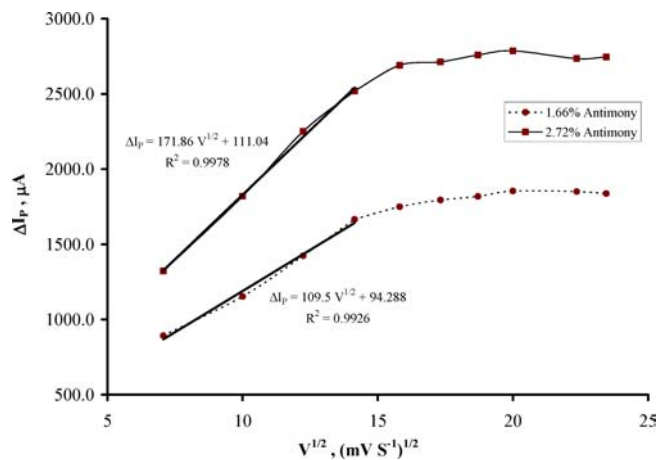


Fig. 5 Influence of scan rate on the peak current and sensitivity. Conditions: Pb–Sb–Sn alloy (Sb wt. 1.66%; Sn wt. 0.24%); sulfuric acid concentration, 4.0 mol L⁻¹; initial potential, -0.70 V; final potential, +0.70 V

Analytical application

A series of standard pb/sb alloy were determined by recommended procedure at the optimum conditions. A linear calibration graph from 0.0056–4.00% antimony was obtained with the correlation equation: $\Delta I_p(\mu A) = (1.0204 \pm 0.09) \times 10^{-3} C_{Sb} - (1.0616 \pm 0.14) \times 10^{-4}$ with $r = 0.9980$ where C_{Sb} is the antimony concentration in percent.

The limit of detection (is equal to three times the standard deviation of the blank peak current divided by the slop of the calibration curve $3S_b/m$) is equal to

Table 1 Determination of antimony in different important and general Pb/Sb alloys

	Various Pb/Sb alloys			
Quantometry Actual (%)	0.540	0.799	1.620	2.370
Proposed method Found (%)	0.5597 ± 0.0311	0.7635 ± 0.0422	1.6536 ± 0.0780	2.3531 ± 0.0251
Recovery(%)	103.6	95.6	102	99.3
RSD%	3.65	-4.44	2.04	-0.72

0.0045%. The relative standard deviation of the method for ten replicate determinations of 1.66 and 2.72% of antimony are 4.6 and 3.2% respectively.

Interference study

In the different important and general Pb/Sb alloys (such as lead-acid battery and electrowinning) concurrently presented negligible amount of As, Cd, Ni, Cu, Se, S, Te, Ag, Al and Bi (lower than 0.03%) that actually haven't any interferences on the analysis. These types of lead alloys usually contain tin (lower than 0.5%). Tin can oxidize in potential region that lead converted to PbSO₄/PbO [18]. The interferences studies show that tin haven't any interfering effect at concentration of lower than 1%.

Determination of antimony in real samples

On the basis of the results obtained from the standards alloys, the recommended method has been successfully applied to the determination of antimony in a series of real samples with various compositions. The results are shown in Table 1. The results are compared with those obtained by Quantometric method. The assessment by Student's *t* test did not show a statistically significant difference between the methods used (95%).

Conclusion

A simple, rapid and selective electrochemical method is proposed as a novel and powerful analytical technique for the solid phase determination of less than 4%

antimony in lead-antimony alloys without any separation and chemical pretreatment. The method is inexpensive and convenient alternative for high costly Quantometric and furnace-atomic absorption spectrometry analysis. The procedure was applied to a variety of real samples to evaluate its effectiveness.

Acknowledgements The authors acknowledge for the Isfahan University of Technology Council for supporting this work.

References

- Pavlov D, Bojinov M, Latinen T, Sandholm G (1991) *Electrochim Acta* 36:2081
- Latinen T, Salmi K, Sundholm G, Monahov B, Pavlov D (1991) *Electrochim Acta* 36:605
- Babic R, Metikos-Hukovic M, Lajqy N, Brinic S (1994) *J Power Sources* 52:17
- Pavlov D, Bojinov M, Latinen T, Sandholm G (1991) *Electrochim Acta* 36:2087
- Metikos-Hukovic M, Babic R, Omanovic S (1994) *J Electroanal Chem.* 374:199
- Hirasawa T, Sasaki K, Taguchi M, Kaneko H (2000) *J Power Sources* 85:44
- Paleska I, Pruszkowska-Drachal R, Kotowski J, Dziudzi A, Milewski JD, Kopczyk M, Czerwinski A (2003) *J Power Sources* 113:308
- Chen HY, Li WS, Zhu YB, Tian LP (2000) *J Power Sources* 88:78
- Rocca E, Steinmetz J (2003) *J Electroanal Chem* 543:153
- Hourigan HF, Robinson JW (1954) *Anal Chim Acta* 10:281
- Detmar DA, Van Der Velde W (1956) *Anal Chim Acta* 15:173
- Tsukahara I, Sakakibara M, Tanaka I (1977) *Anal Chim Acta* 92:379
- Adams F, Hoste J (1962) *Talanta* 9:827
- Adams F, Hoste J (1963) *Talanta* 10:1093
- Neef J De, Adams F, Hoste J (1972) *Anal Chim Acta* 62:71
- Murti SS, Rajan SCS (1988) *Talanta* 35:443
- Harmse MJ, McCrindle RI (2002) *J Anal At Spectrom* 17:1411
- Petersson I, Ahlberg E (2000) *J Power Sources* 91:143