

# A lead–film electrode on an aluminium substrate to serve as a lead–acid battery plate

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## Abstract

Compact lead layers have been deposited on the surfaces of aluminium and aluminium alloys. These coatings are uniform in thickness and have high porosity. The lead–film electrode produced on aluminium plate can be used as the positive electrode in a lead–acid battery. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Aluminium substrate; Lead–acid battery; Lead film; Battery plate

## 1. Introduction

This study extends attempts [1] to improve the performance of the lead–acid battery. The earlier work was mainly devoted to investigations of lead–film electrodes on copper and copper-coated titanium substrates. It was found that lead-covered copper grids can be used as the positive electrodes in lead–acid batteries and allow high values of discharge current density to be obtained.

The aim of the present investigation is to study the electrochemical characteristics and free corrosion rate of aluminium-based, lead–film electrodes and to characterize the solid products of interaction between the aluminium and the lead-containing melt, as well as those of interaction between the lead coating and sulfuric acid.

## 2. Deposition of lead coating

The deposition of continuous lead coatings on aluminium from aqueous solutions is practically impossible because of the dense film of oxide which is always present on the aluminium surface [2]. Apparently, the formation of lead–film electrodes on aluminium from a molten-salt electrolyte is the only practical method. Since aluminium is virtually insoluble in liquid lead, even at 900°C [3], the resulting coating will consist of pure lead.

Electron micrographs of a lead deposit on aluminium are presented in Fig. 1, together with corresponding X-ray phase analyses using  $Pb M\alpha_1$  rays. Micrograph A1 shows that the lead layer has numerous pores (diameter, 3–10  $\mu\text{m}$ ) through the coating that reach the aluminium base. In micrograph B1, the coating has a continuous uniform thickness which features very fine porosity with pore diameters of around 0.2  $\mu\text{m}$ . This lead plate is shiny and electrochemical investigations reveal that the discharge current density does not exceed 70  $\text{mA cm}^{-2}$ . Thus, a special study was conducted to form a lead coating with a developed surface of high surface roughness (micrograph C1). The thickness of this film on the aluminium substrate was determined by a direct metallographic method and by lead etching in a concentrated solution of nitric acid. Both methods found that the lead coating had a uniform thickness of between 100 and 500  $\mu\text{m}$  depending on the coating conditions. The lead coating exhibits good adhesion with the aluminium surface (Fig. 2). According to X-ray phase analysis, the thickness of the film is uniform and is permeated by numerous fine pores of diameter 0.2 to 0.5  $\mu\text{m}$  that do not reach the metal base. All further studies were conducted on this lead/aluminium electrode with a rough surface and fine porosity.

## 3. Experimental

The lead layers were deposited on to smooth plates of aluminium (99.99% Al) or aluminium alloy AD1 (total

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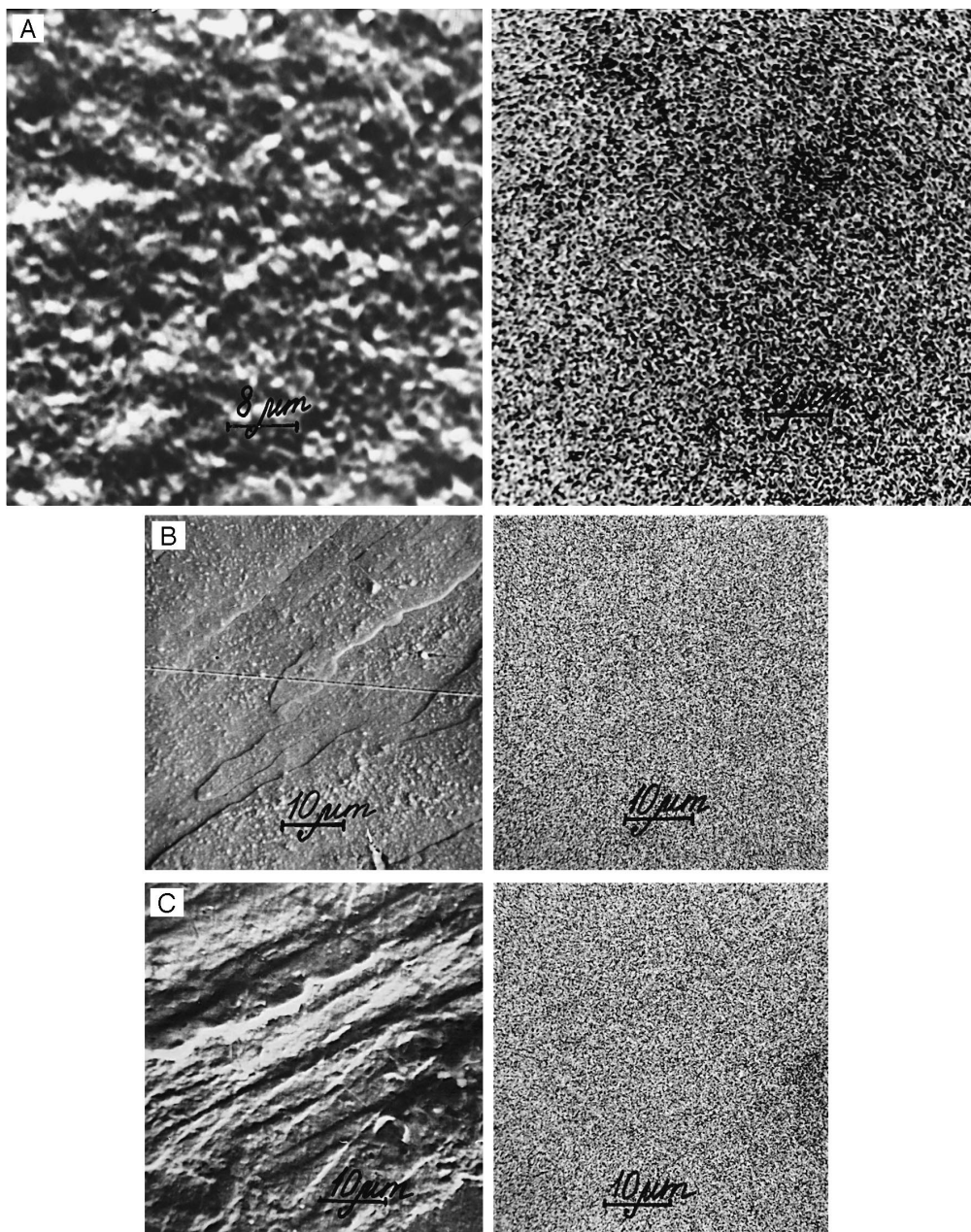


Fig. 1. Surface images of lead film on aluminium surface. A1, B1, C1: scanning electron micrographs. A2, B2, C2: X-ray phase analysis with  $\text{Pb M}\alpha_1$  rays. (A): film with large pores ( $\times 800$ ). (B): film with fine pores, i.e., shiny coating ( $\times 1000$ ). (C): rough surface coating ( $\times 1000$ ).

impurities = 1 wt.%). The latter is mechanically stronger than pure aluminium. The thickness of the uncoated aluminium plates was  $200\ \mu\text{m}$  and the apparent surface area was  $4\ \text{cm}^2$ . Lead deposition was carried out without any preliminary treatment of the substrate such as pickling or de-oiling; the aluminium specimens were simply immersed in molten electrolyte at a set temperature. The exposure time of the aluminium plates in the halide melts varied from 10 s to 2 min. It was possible to coat several specimens simultaneously. The resulting coating was washed thoroughly to remove salts.

Electrochemical measurements of half-immersed lead/aluminium electrodes were performed in a standard electrochemical cell under argon atmosphere at temperatures between 20 and  $30^\circ\text{C}$ . In all cases,  $4.57\ \text{M}\ \text{H}_2\text{SO}_4$  was used as the electrolyte. A layer of lead dioxide was deposited on the electrodes during the first two cycles at 2.0 V in  $4.57\ \text{H}_2\text{SO}_4$ . Cycling of the lead-film electrode was conducted under potentiodynamic conditions with a linear scanning rate of  $10\ \text{mV}\ \text{s}^{-1}$  and a holding time of 200 s at the potential limits. The rate of free corrosion of lead/aluminium electrodes was determined by a gravimet-



Fig. 2. Cross-section ( $\times 100$ ) of lead-film electrode before cycling.

ric method. No less than five electrodes were tested in each series. Errors in the values of the electrochemical parameters and corrosion rate did not exceed 5 and 10%, respectively.

#### 4. Results

Typical current-potential curves for lead-film electrodes are shown in Fig. 3. The fact that the discharge current density increases with cycling may be easily explained by conversion of lead into a layer of lead dioxide. More cycles are required for dioxide layer formation on an aluminium surface than on a copper surface because of the much larger thickness of the lead coating on the former substrate. The value of the discharge current density reaches a maximum after 6 to 8 cycles and then remains constant during next 300 cycles. Neither a change in the substrate material (Fig. 4) nor an increase in the test temperature up to  $30^{\circ}\text{C}$  (Fig. 5) causes any significant influence on the values of the discharge current density.

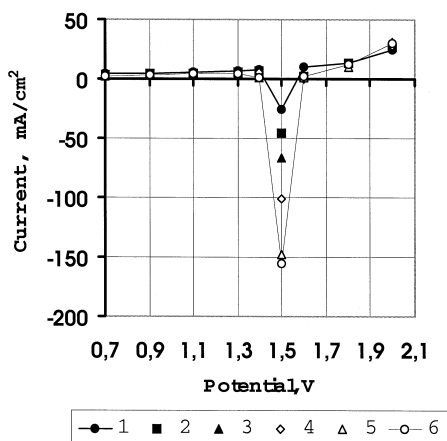


Fig. 3. Voltammograms between 0.7 and 2.0 V (vs. Ag/AgCl reference electrode) for a lead/aluminium electrode in  $4.57\text{ M H}_2\text{SO}_4$  at  $20^{\circ}\text{C}$ .

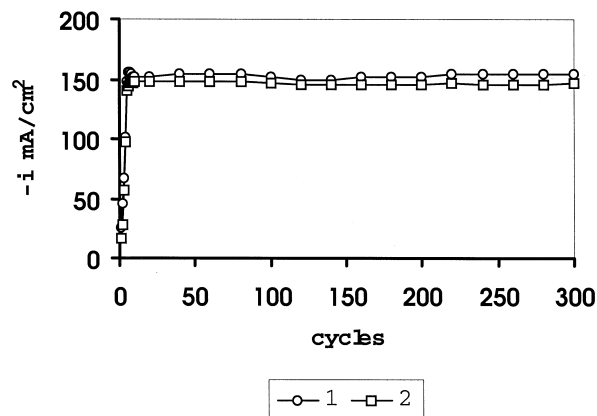


Fig. 4. Change in peak current density during voltammetric scan of a lead-film electrode on: (1) aluminium plate; (2) aluminium alloy.

After 200 cycles, the scanning voltammetry was stopped and a rest period of 12 h was introduced. Scanning was then recommenced for about 100 cycles. During the first cycle after the rest period, the current density was slightly low, but it then increased and returned exactly to its former value. The discharge current peak occurs at a potential of 1.5 V (relative to a Ag/AgCl reference electrode). No shift in this potential was observed during cycling.

After electrochemical testing, the concentration of  $\text{Al}^{3+}$  ions in the acid solution was monitored by means of a Perkin Elmer atomic absorption spectrometer. No escape of  $\text{Al}^{3+}$  ions through the pores of the lead coating into the sulfuric acid was observed. In addition, there was no shedding of lead from the electrodes during prolonged electrochemical cycling. Thus, it is evident that the adhesion of the lead coating is extremely good.

The corrosion rate of the lead/aluminium electrodes was determined in acidic solution without any polarization during a period of 168 h (1 week). The rate was determined both by a weight-loss method and by an analytical method and was  $7 \times 10^{-6}\text{ g cm}^{-2}\text{ h}$  and  $1.6 \times 10^{-5}\text{ g/l}$ , respectively. This treatment without polarization did not

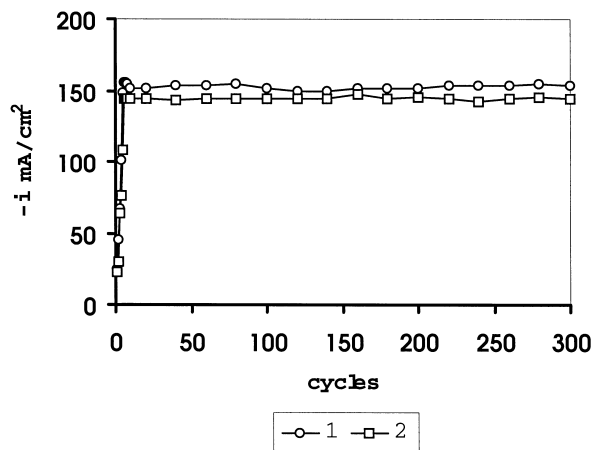


Fig. 5. Change in peak current density during voltammetric scan of a lead-film electrode on an aluminium substrate at: (i)  $20^{\circ}\text{C}$ ; (2)  $30^{\circ}\text{C}$ .

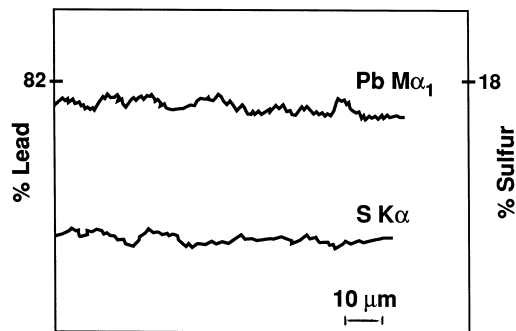


Fig. 6. Profiles of lead and sulfur distribution on surface of lead/aluminium electrode after 300 cycles (1:1).

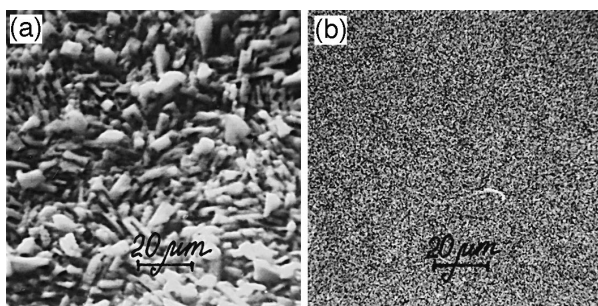


Fig. 7. Surface image of lead/aluminium electrode after 300 cycles ( $\times 2000$ ): (a) scanning electron micrograph; (b)  $\text{Pb M}\alpha_1$  rays.

produce any bulking, shedding or scaling of the active lead dioxide mass.

Micro-X-ray spectrometric data revealed that after 300 cycles, a homogeneous distribution of lead and sulfur was present on the surface of the lead film (Fig. 6). There was no formation of coarse lead sulfate crystals (Fig. 7) and the sulfate layer produced during prolonged cycling did not impede further discharge.

## 5. Discussion

It has been found that aluminium is a promising substrate for positive-plate grids in lead–acid batteries for the following reasons.

(i) The specific gravity of aluminium is 4.2 times less than that of lead, and 3.3 times less than that of copper.

(ii) The electrical conductivity of aluminium is 1.5 times less than that of copper, but 7.8 times more than that of lead.

(iii) The lack of aluminium corrosion through the pores of the lead coating increases the useful life of the positive electrode and prevents scaling of the active lead dioxide mass through destruction of grid.

(iv) There is an attractive relationship between the specific gravity and the price of aluminium as compared with other possible substrate materials.

The contact-exchange method used for formation of lead–film electrodes on different metallic substrates in a molten-salt electrolyte is extremely simple. It merely involves immersing the electrode in the melt at a definite temperature, holding it there for a few minutes, withdrawing the coated sample, and then washing it in water to remove the salts. There have been no published reports of the quality of lead coatings obtained from aqueous solutions, especially with respect to good adhesion with an aluminium substrate.

The above studies show that by varying the conditions of both preparing the molten-salt electrolyte and performing the deposition, a lead coating can be formed on an aluminium surface to have high electrochemical activity and good corrosion characteristics. Moreover, there is no deterioration in these electrochemical characteristics during prolonged cycling; the lead/aluminium electrode has the same appearance after 300 cycles as after 10 cycles. It seems likely that this cycle-life can be significantly increased.

## 6. Conclusions

The use of aluminium and aluminium alloys as grids for positive electrodes can increase the life expectancy of lead–acid batteries. If both positive and negative electrodes are produced on an aluminium base, it is possible to decrease substantially the weight of the battery and increase the specific energy by 30 to 35%.

## References

- [1] L.A. Yolshina, V.Ya. Kudyakov, V.G. Zyryanov, *J. Power Sources* 65 (1997) 71–76.
- [2] L. Young, *Anodic oxide films*, Energy Press, Leningrad, 1967, p. 232.
- [3] F.A. Shunk, *Constitution of Binary alloys*, 2 suppl., Metallurgy Press, 1973, p. 759.