

Preparation of lead-sodium alloy by fused salt electrolysis using beta alumina

M Kamaludeen, K Balakrishnan

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

and Gurdeep Singh

Indian School of Mines, Dhanbad, INDIA

The electrolytic method of preparing lead-sodium alloy from the eutectic melt of NaCl-ZnCl₂ at 623K using molten lead cathode and sodium ion conducting beta alumina solid electrolyte as diaphragm has been investigated. The characteristics of the alloy, like hardness, microstructure and its polarisation behaviour in battery grade 10N H₂SO₄ are studied and compared with that of pure lead.

Key words: Lead sodium alloy, beta alumina, fused salt electrolysis

INTRODUCTION

The use of solid electrolyte separators in the electro-deposition of metals by fused salt electrolysis is one of the promising approaches envisaged for the selective deposition of metals.

β -alumina, a Na⁺ ion conducting solid electrolyte which finds tremendous application in the development of high energy density batteries and power sources has been used for the deposition of Na on molten Pb cathode to form Pb-Na alloy from fused salt baths [1].

EXPERIMENTAL

The experimental cell consisted of a glass cell protected by outer glass jacket, being externally heated by a resistor furnace operating at temperature upto 773K with controller. Provision has been made for the introduction of anode, cathode, reference electrode, thermocouple and line for chlorine, argon gases as already described [2].

About 100 g of premelted eutectic mixture of NaCl-ZnCl₂ was taken in a glass cell and slowly heated under vacuum. Residual moisture removal was accomplished by chlorination accompanied by argon bubbling [3]. The temperature of the melt was maintained at 623K measured by a glass sheathed chromel-alumel thermocouple and the experiment was conducted with argon gas flowing above the melt. One end closed tube of β -alumina (1 cm o.d, 9 cm long) containing 10 g of Pb (AR) was slowly introduced into the melt to a depth of 2 cm with the support of a glass holder. Special care was taken to prevent thermal shock to the β -alumina tube by slow equilibration of the temperature. Electrical contact to molten Pb was provided by means of 0.5 mm thick W wire lead sheathed in glass

tubing. Spectral pure graphite rod of 5 mm dia was introduced into the melt to serve as the counter electrode. Deposition of Na on molten Pb cathode was accomplished by constant current electrolysis at 300 mA for 2 h at cell voltage of 3.5-3.75 V, with anodic and cathodic current densities of 100 and 50 mA cm⁻² respectively. Alloy formed inside the β -alumina tube was cast in the form of 8 mm dia rod in graphite mould and was tested for Na content by flame photometry and Zn by chemical analysis.

POLARISATION

Polarisation behaviour of Pb and its alloys has been studied widely [4,5]. Pb-Na alloy formed in this experiment was subjected to potentiodynamic polarisation in 10N H₂SO₄ after diluting the alloy with excess Pb so as to make the Na content to 0.9 w/o. Voltammogram was recorded by varying the electrode potential from -1.3 to +1.55 with reference to Hg/Hg₂SO₄ electrode and Pt as counter electrode at sweep rate of 3 mV.s⁻¹. Similar voltammogram was recorded for pure Pb also for a comparative study.

Micrograph of Pb-Na alloy containing 0.9 w/o Na and pure Pb were taken under SEM and microhardness was determined by indentation method.

RESULTS AND DISCUSSION

Na content in the alloy is found to be 3.153 w/o. Zn is absent, indicating the discharge of Na⁺ ion only. As β -alumina is specific to Na⁺ ion migration, it may be established that under conditions of electrolysis, Na⁺ ion alone can diffuse through β -alumina and get discharged as Na metal on Pb cathode. In situ alloying of Na with Pb is facilitated by the faster diffusion mechanism due to the liquidous nature of the cathode.

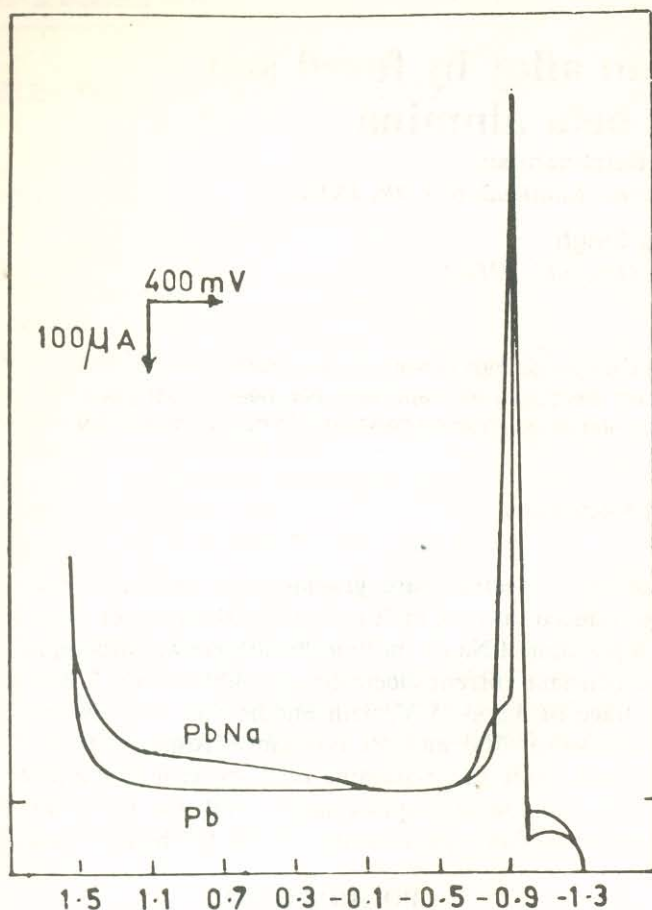


Fig. 1: Voltammogram of Pb and Pb-Na in 10N H_2SO_4 vs Hg/Hg_2SO_4 , $3 \text{ mV} \cdot \text{s}^{-1}$

From the polarisation curve shown in the Fig. 1, it is inferred that the initial cathodic current due to H_2 evolution decreases continuously and then the anodic current due to oxidation of Pb into Pb^{2+} ion is observed. Both curves display peaks at potential corresponding to the equilibrium value of $Pb/PbSO_4$ formation by dissolution precipitation mechanism [6]. Beyond the maximum, the current drops to a low value. It is observed that the anodic current due to $PbSO_4$ formation is more for Pb-Na alloy than for pure Pb. The passivation current at 0.8V is also about three times more for Pb-Na alloy indicating a much higher rate of corrosion in the passive state, i.e. less

inhibitive nature of the passive film. This may be due to the larger number of intercrystalline spaces in the original film for Pb-Na alloy than for pure Pb.

The microhardness of Pb-Na alloy has increased six times (36 kg mm^{-2}) when compared to that of pure Pb (6 kg mm^{-2}) due to the presence of 0.9 w/o Na and this may be attributed to the uniform distribution of needle shaped intermetallic crystals of Pb-Na alloy as depicted in the scanning electron microscope (Fig. 2).



Fig. 2: Microstructure of Pb-Na

REFERENCES

1. G J May, *J Power Sources*, **3** (1978) 1
2. M Kamaludeen, K Balakrishnan, N S Rawat and Gurdeep Singh, *Trans SAEEST*, **21** (1986) 1
3. D L Maricle and D N Hume, *J Electrochem Soc*, **107** (1960) 354
4. G Archdale and J A Harrison, *J Electroanal Chem*, **34** (1972) 21
5. B K Mohanto, *J Electrochem Soc*, **126** (1979) 365
6. M Saho and M Okamoto, *J Electrochem Soc*, **110** (1963) 605