

PRECONDITIONING OF LEAD-SILVER ALLOY ANODES FOR USE IN ELECTROWINNING OF METALS

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Lead alloys are customarily used in the electrowinning of metals like zinc, copper and chromium. Anode corrosion is one of the problems associated with the lead anodes and it can be reduced by preconditioning the lead anodes and it can be reduced by preconditioning the lead anodes suitably prior to the use in the electrolytic cells. The preconditioning involves anodic treatment of lead electrodes in fluoride solution, where a compact adherent layer of lead dioxide is built up relatively in a shorter time. The anodic films formed under different conditions of the pretreatment process have been characterised by polarisation measurements. A passive film of lead fluoride is formed initially followed by propagation of PbO_2 . The role of fluoride ion in the formation of lead dioxide is discussed. Fluoride ion is well known for its surface activity and lead dioxide which nucleates over the passive film of PbF_2 tends to be adherent, protecting the underlying lead effectively during the use in metal winning cells.

Keywords: Lead alloy anode, preconditioning, polarisation and lead dioxide.

INTRODUCTION

In the electrowinning of zinc, copper and chromium it is customary to use an alloy of high purity lead containing 0.5 to 1% silver as the anode material. During initial stages of the electrolysis the reaction at the anode is the formation of PbO_2 . Once a compact lead dioxide is built up the evolution of oxygen occurs. In the initial stages the lead dioxide film is loosely attached to the anode surface and frequently falls to the bottom of the cell. Part of the anode mud is suspended in the electrolyte as fine particles and incorporated in the cathode deposit. This kind of anode corrosion can be reduced by preconditioning the anodes suitably prior to use in electrolytic cell. The pretreatment involves anodic treatment of lead alloy electrodes in fluoride or fluoride/sulphate solution where a compact adherent layer of lead dioxide is built up relatively in a shorter time.

Patent informations relating to this preconditioning describe various process parameters like fluoride concentration, current density, duration of treatment [1]. However, an insight into the basic aspects of the electrode processes responsible for the build up of corrosion resistant surface oxides has not been obtained so far. In this paper some contributions have been made for characterisation of the films formed under different conditions of the pretreatment process. The role of fluoride ion in improving the mechanical properties of lead dioxide growth and the effects of different

parameters like anode potential and fluoride concentration on nucleation of lead dioxide on the electrode surface have been examined.

EXPERIMENTAL

Lead-silver (1%) alloy was cast in the form of rod and embedded in a teflon rod so as to give a surface area of 1 cm^2 . It was used in the potentiostatic and potentiodynamic studies carried out employing a Wenkin potentiostatic and an x-y recorder. An H- type glass cell of 200 cm^3 capacity was used. The auxiliary electrode was a platinum foil.

A saturated calomel was used as the reference electrode and all potentials were quoted with respect to it.

Analar grade KF was used for preparing fluoride solutions.

RESULTS AND DISCUSSION

Preconditioning in the present context is concerned with surface oxidation of lead under high anodic polarisation conditions where oxygen is also evolved simultaneously. The electrochemistry of this surface process partly centres around the formation of PbF_2 whose solubility or crystallisation on the electrode surface are greatly influenced by fluoride concentration in the electrolyte and polarisation conditions in the pretreatment step. Characterisation of this anodic film becomes important in view of its conversion on further

oxidation to PbO_2 whose mechanical properties decide the corrosion resistance of the anode material.

Anodic polarisation curves as obtained by the potentiodynamic method is given in Fig. 1 for different concentrations of fluoride. The lead alloy exhibits an active passive behaviour with fairly wide potential range of passivation. An anodic peak seen around -0.45V is due to lead fluoride formation. The passivating potential, E_p , varies with fluoride concentration and becomes more positive a decrease in concentration of fluoride. However the critical current for passivation, I_c passivation current, I_p , decrease with decrease in concentration of fluoride. These facts indicate that fluoride ion is involved in the passive film formation. At high fluoride concentrations the rapid dissolution of the lead alloy leads to super saturation and precipitation even at lower potentials. However the film seems to be porous as indicated by high I_c and I_p . At lower concentrations of fluoride more compact films are formed as indicated by low I_c and I_p . As a result of PbF_2 formation on the surface the electrodes exhibit a wide potential range of

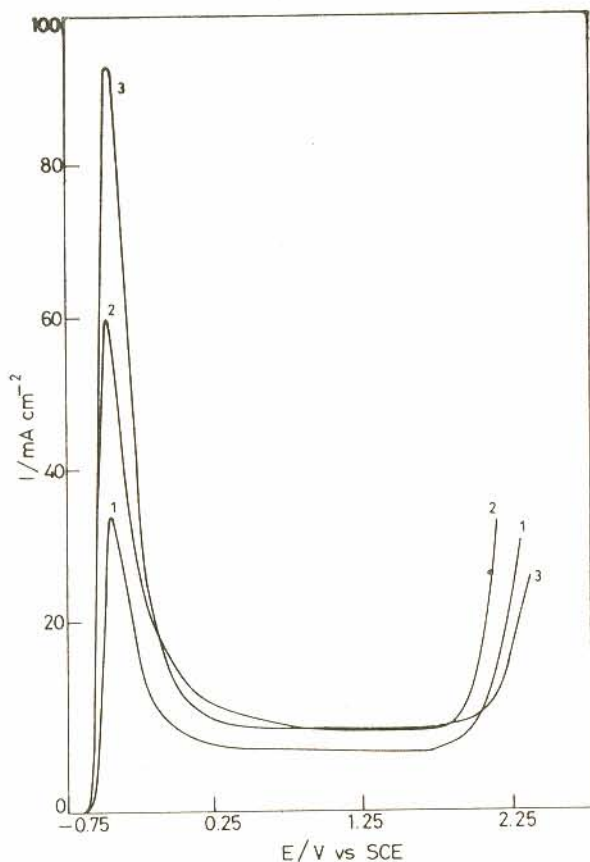


Fig. 1: Effect of concentration of fluoride on the anodic sweep of Pb-1% Ag at 10 mvs^{-1}
(1) 10 g l^{-1} (2) 20 g l^{-1} (3) 50 g l^{-1}

passivation from 0.3V to 2V and this region is extended further for higher fluoride concentrations and oxygen overpotential is substantially increased. This aspect assumes significance when one compares the passivation of Pb-Ag alloy in fluoride solution with that in sulphate solution as illustrated in Fig. 2. The concentrations of fluoride and sulphate are equal. It may be observed that the critical current, the passivation current and the charge under the passivating peak are much lower for sulphate solution and it indicates the extent of formation of films like PbSO_4 and PbF_2 in their respective electrolytes. PbF_2 by virtue of its higher solubility grows to a higher thickness and higher oxygen overpotential in fluoride solution is due to these passive layers which contribute significantly to the ohmic character of these films.

A series of potentiostatic current-time curves for the anodic treatment are plotted in Fig. 3. A sudden initial increase in current is due to dissolution of lead to form PbF_2 which imposes transport limitations and a current minimum is reached. Then the current increases gradually as more and more PbO_2 is nucleated from the PbF_2 phase. Higher rate of current increase at the more positive potential indicates the potential dependent nucleation in the reactivation of the electrode surface through propagation of PbO_2 . The formation of PbO_2 requires higher overpotential and it occurs at a faster rate when the anode potential is increased.

The effect fluoride concentration on the growth of PbO_2 is shown in Fig. 4. The rate at which current increases for PbO_2 growth is more as fluoride concentration increases. When the propagation of lead dioxide is complete oxygen continues to evolve on the PbO_2 sites. The dependence of PbO_2 growth on

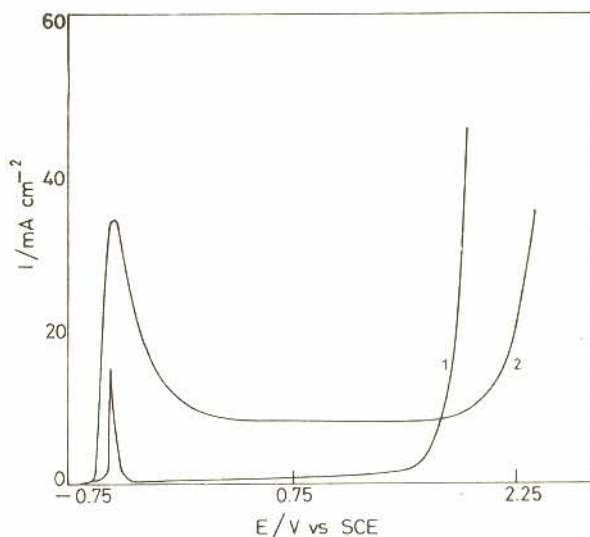


Fig. 2: Potentiodynamic curves for Pb-1% Ag in
(1) $0.5 \text{ M Na}_2\text{SO}_4$ and (2) 0.5 M KF at 10 mvs^{-1}

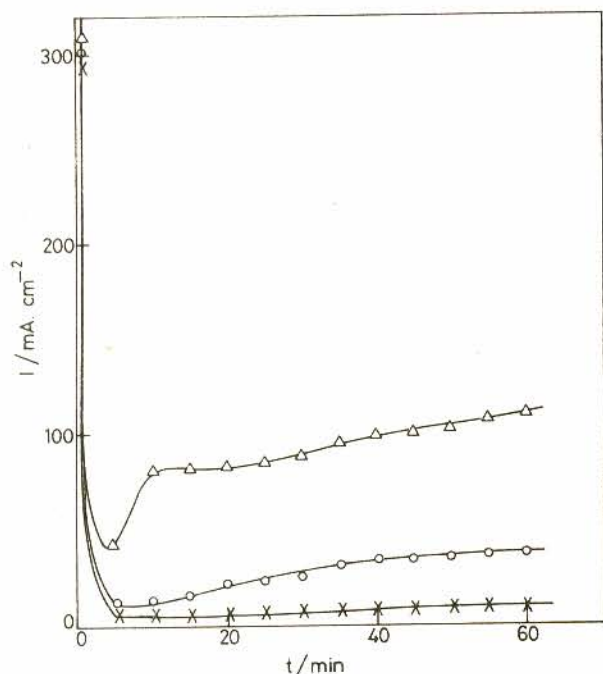


Fig. 3: Current time transients for anodic treatment of Pb-1% Ag in 20 g l⁻¹ fluoride solution at (*-*) 1.6 V (0-0) 1.8 V and (Δ-Δ) 2.0 V vs SCE

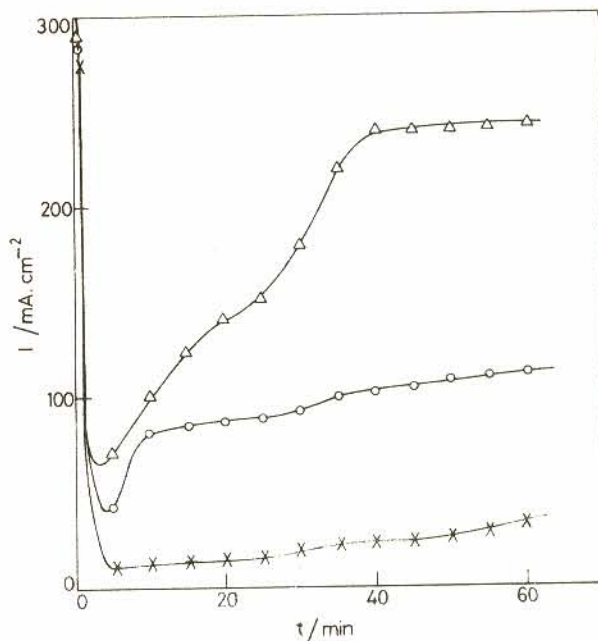
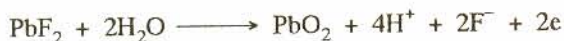


Fig. 4: Current-time transients for anodic treatment of Pb-1% Ag at 2.0 V vs SCE in (Δ-Δ) 50 g l⁻¹ (0-0) 20 g l⁻¹ and (*-*) 10 g l⁻¹

fluoride concentration is related to the amount of PbF₂ formed, nature of its crystallisation and its solubility under different fluoride concentrations. At lower fluoride concentrations crystallisation of PbF₂ on the surface is delayed and the reaction Pb-Pb²⁺ proceeds at a low rate, resulting in lower rate of PbO₂ nucleation and its growth.

Fluoride ion by virtue of its surface active nature, adsorbs on the electrode surface under anodic polarisation conditions and corrodes it uniformly to form surface layers of PbF₂ which are subsequently oxidised to PbO₂.



The PbF₂ film bridges the overlying PbO₂ layers effectively to the substrate lead, facilitating PbO₂ growth in a compact form.

This kind of initial rapid dissolution and subsequent formation of thicker surface layers could not be achieved in sulphate solutions which are normally employed in electrowinning of metals. PbSO₄ is nearly 15 times less soluble than PbF₂. Conversion of PbSO₄ to PbO₂ results in a 48% decrease in volume creating porosity and facilitating

diffusion of oxygen. Russian workers have demonstrated that anodic corrosion of lead is based on the diffusion of atomic oxygen through PbO₂ layer [2].

Thicker surface layers are possible with fluoride electrolyte, which are subsequently converted to a massive deposit of PbO₂, protecting underlying lead during its use in metal winning cells. The lead dioxide thus formed is so hard and adherent that it can only be removed by an emery wheel or similar means.

CONCLUSION

Potentiostatic and potentiodynamic studies indicate that preconditioning involves initial formation of a passive film of PbF₂. By virtue of its higher solubility, the initial anodic film of PbF₂ builds up to a higher thickness on the surface, resulting in a massive growth of PbO₂ on further oxidation in a short time. Thus anode corrosion of lead can be reduced by preconditioning in fluoride solution prior to use in electrolytic cells.

REFERENCES

1. *Canad Pat No 743 923* (1966).
2. B N Kabanov, E S Weisberg, I L Romanova and E V Krivalopova, *Electrochim Acta*, **9** (1964) 1197