

Anodic behaviour of lead in gelled sulphuric acid electrolyte—A cyclic voltammetry study

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The anodic behaviour of Pb in gelled sulphuric acid electrolyte has been studied and compared with that in flooded electrolyte using cyclic voltammetry. The oxides formed in both the electrolytes have been examined using X-ray diffraction. It is found that the oxide formation takes place at a less positive potential in gel electrolyte possibly due to the predominant presence of basic sulphates and formation of α -PbO₂ in the film. This is substantiated by the X-ray diffraction studies. Consequently the overpotential for evolution of oxygen is also reduced.

Key words: Anodic polarisation of lead, gelled electrolyte, cyclic voltammetry

INTRODUCTION

Gelled electrolyte batteries accept charge at a potential which is considerably low compared to that fixed for flooded electrolyte cells. The batteries get charged at a lower potential due to the depolarisation of the negative electrode by the oxygen recombination reaction and easier conversion of lead sulfate to lead dioxide [1]. The behaviour of the Pb/lead oxide/sulphuric acid system has been studied both in flooded and gelled acid electrolyte to establish the mechanism for the anodic reaction.

EXPERIMENTAL

Pure lead rods (Johnson Matthey) mounted in teflon were used as electrode. This was first emery polished, degreased in trichloroethylene, and electrochemically polished in perchloric acid. Analytical grade reagents were used for preparing the electrolyte [2]. The strength of the acid in both cases was 8.6N. A Wenking Potentiostat Model POS 73 in conjunction with a Rikadenki X-Y Recorder was used for cyclic voltammetry (C.V.) experiments. Potentials referred to are all with respect to Hg/Hg₂SO₄ reference electrode. The electrodes were initially oxidised at +1450 mV in the respective electrolytes and then scanned between +850 and +1350 mV and +850 and +1450 mV.

RESULTS AND DISCUSSION

The typical cyclic voltammograms obtained are given in Figs. 1 and 2. It is found that the oxidation reaction, oxygen evolution as well as reduction of PbO₂ to PbSO₄ take place at less positive potentials in the case of gelled electrolyte. The anodic and cathodic peak currents are also lower in the case of gelled electrolyte. The reduction peak shows tailing which is more predominant at higher scan rates.

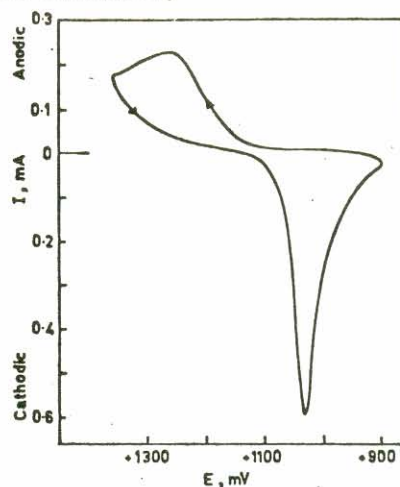


Fig. 1: Cyclic voltammogram of pure lead electrode in silica based gel electrolyte. Scan rate = 25mV.min⁻¹

It has been established that α -PbO₂ is formed at a lower overpotential and also that oxygen overpotential is lower on α -PbO₂ [3]. Moreover, tet. PbO and basic sulphates get oxidised earlier than PbSO₄ [4]. The lower overpotential for oxygen evolution as well as oxide formation indicates that the anodic film in gel electrolyte consists of predominantly basic sulphates as well as α -PbO₂. This is substantiated by the XRD studies (Fig. 3) of the oxide formed in both gel and sulphuric acid electrolytes. The oxide formed in gel electrolyte contains both α - and β -PbO₂, the former being predominant along with basic sulphates. In the case of flooded electrolyte both α - and β -PbO₂ are present, the latter being predominant.

It is well established that alkaline conditions favour α -PbO₂ formation. Development of alkaline condition at the electrode/electrolyte interface, formation of basic sulphate and the potential shift noticed can be attributed to the supersaturation of the interface caused by the decreased rate of transfer of Pb(II) ions as well as of water

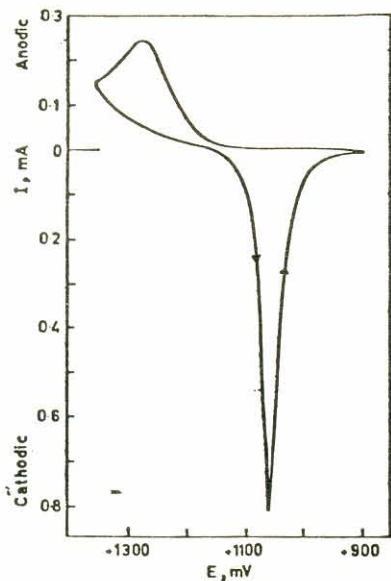


Fig. 2: Cyclic voltammogram of pure lead electrode in sulphuric acid electrolyte. Scan rate = $25\text{mV}\cdot\text{min}^{-1}$

formed during cathodic reduction of PbO_2 to PbSO_4 in gel electrolyte. Decrease in i_p in gel electrolyte also indicates the lower concentration of sulphate ions which is due to restricted mass transfer in gel electrolyte.

CONCLUSION

Due to the restricted mass transfer in gel electrolyte, higher pH develops at the electrode-electrolyte interface. This favours formation of surface films consisting predominantly of $\alpha\text{-PbO}_2$ and basic sulphates. This influences the kinetics of gas evolution and also the course of oxidation-reduction reaction at the interface.

REFERENCES

1. B L McKinney, B K Mahato and K R Bullock in

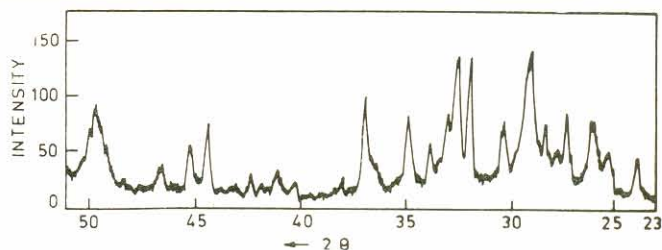


Fig. 3(a): Diffractogram of oxide formed on lead in gelled sulphuric acid

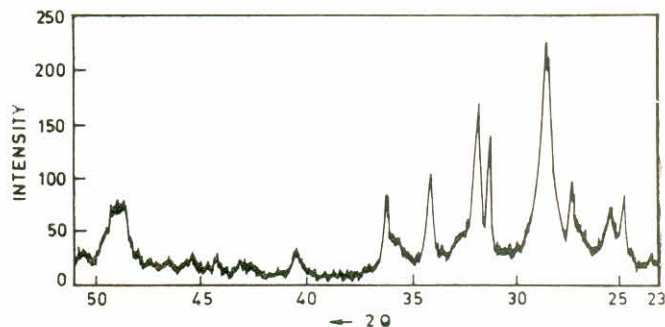


Fig. 3(b): Diffractogram of oxide formed on lead in sulphuric acid

Advances in Lead Acid Batteries, (Ed) K R Bullock and D Pavlov, Vol. 84, The Electrochemical Society Inc. (Pennington, N.J.), (1984)

2. P C Wariyar and P V Vasudeva Rao, *Bull Electrochem*, 4 (1988) 731
3. W Visscher, *J Power Sources*, 1 (1977) 257
4. D Pavlov, *Power Sources for Electric Vehicles*, (Ed) B D McNicol and D A J Rand, Elsevier, Amsterdam (1984)