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OXIDATION AND REDUCTION PROCESSES OF LEAD IN pH 9 TO 14 SOLUTIONS

by

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ABSTRACT

The oxidation and reduction processes which take place at Pb electrodes in aqueous alkaline solutions have been studied by cyclic voltammetry and potential step techniques in this work. The initial stages of lead oxidation in a range of alkaline solutions of varying pH and ion content have been found to show strong similarities. In both carbonate and borate buffered solutions (pH > 9), and in more alkaline solutions, Pb oxidation commences at a potential of ca. 140 mV vs. RHE. In pH 14 solutions, $Pb(OH)_2$ is soluble, hence producing $Pb(OH)_3^-$ and only a small amount of a stable surface film. At lower pH's, $Pb(OH)_2$ is not predicted to be soluble, and in borate-buffered solutions, a stable, reducible $Pb(OH)_2$ film appears to form. In carbonate- buffered solutions, unusual electrochemical behaviour was observed.

It is suggested that, in these carbonate-containing solutions, some $Pb(OH)_2$ is transformed to an adherent Pb/oxide/carbonate phase, which is difficult to remove electrochemically in a normal cathodic sweep. The film can be reduced at very negative potentials. Also, the surface film which is formed by potential holding at the positive potentials, can be reduced. A model for the early stages of lead oxidation in carbonate solutions is presented.

Scanning Electron Microscopy has been utilized to study the effect of various electrode pretreatments on the cycling behaviour of lead in carbonate solutions. It has also been used to analyse anodic deposits formed during electrochemical experimentation. It was found that two types of electrochemical response occur depending on the condition of the surface of the lead electrode. The results are correlated with photomicrographs.

Other surface analytical techniques such as Auger Electron Spectroscopy have also been utilized to examine the anodic films formed on a lead electrode in carbonate-containing solutions.