THE CORROSION BEHAVIOUR OF LEAD IN SODIUM HYDROXIDE SOLUTIONS CONTAINING MOLYBDATE IONS

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SUMMARY

The corrosion rate and potential of lead were measured in 0.2–2M NaOH solutions containing 10^{-4}–5×10^{-1}M Na_2MoO_4. Results showed that the corrosion rate and potential decrease with increase of molybdate concentration.

This indicated the deceleration of the cathodic reaction. Anodic polarisation showed that the increase of MoO_4^{-2} concentration delays the onset of passivity.

Cathodic polarisation curves were also measured; the results confirmed the deceleration of the cathodic reaction with increase of molybdate concentration.

INTRODUCTION

Brasher[6] suggested that some anions are corrosive when present in large dilution and become inhibitive at high concentrations. In testing this theory the corrosion behaviour of lead in sodium hydroxide solutions containing sodium phosphate and sodium chromate were previously studied[1–2]

In this work we studied the corrosion behaviour of lead in alkaline molybdate solutions.

EXPERIMENTAL

The polarisation measurements on the lead electrode were carried out in a cell described in an earlier publication[3]. This cell is constructed from the arsenic–free hard borosilicate glass, Hysil, and thus it perimits the vigorous purification of the solutions under investigation thro ughpre–electrolysis. For this purpose we used a platinum electrode (2 cm² platinum sheet weldet to a platinum wire sealed to glass).

The electrode were prepared from extra–pure lead rods 3 mm in diameter (Shering Kahlbaum Company). The electrode area was 1cm². Each run was carried out with a new electrode. All solutions were prepared from A.R. materials. Before each run, the cell was cleaned with a mixture of nitric and sulphuric acids (A.R.) and thoroughly washed with conductance water.

Determination of the corrosion rate was carried out using the weight–loss technique. Experiments were performed on pieces of lead of area 6.25 cm² and 0.8 mm thick, cut from analar lead sheet. The test pieces were first degreased with acetone, washed with conductivity water, dried in alcohol and ether, and then weighed.

Corrosion tests were carried out in a wide 30 ml. jar, in which the specimen was suspended for 2 hours in the test solution. The specimen was then removed, rinsed with conductivity water and finally dried and weighed.

All corrosion tests were carried out in aerated, unstirred solutions, results were duplicated and the mean was computed.

For measuring the corrosion potential, the potential of the lead electrode was followed as a function of time over a period of 3 hours. In all solutions studied the potential became constant with Ca. 2 hours. All measurements were carried out at 30°C in an air thermostate controlled to ± 5°C.

Results and Discussion:

The potential of the lead electrode was measured in 0.2–2M sodium hydroxide solutions.

In Fig. (1) the steady state potentials, observed three hours after immersion, are plotted as a function of the pH values of the solutions. The dotted lines in this figure represent the theoretical potential / pH relations of the Pb / PbO and Pb / H PbO$^-_2$ systems. These systems are characterised by standard potentials (at 1M OH)[5] of –0.580 and –0.540 volt respectively. It is clear from Fig. (1) that the experimental values coincide fairly with that of the Pb / PbO couple. Hence the anodic reaction is represented by
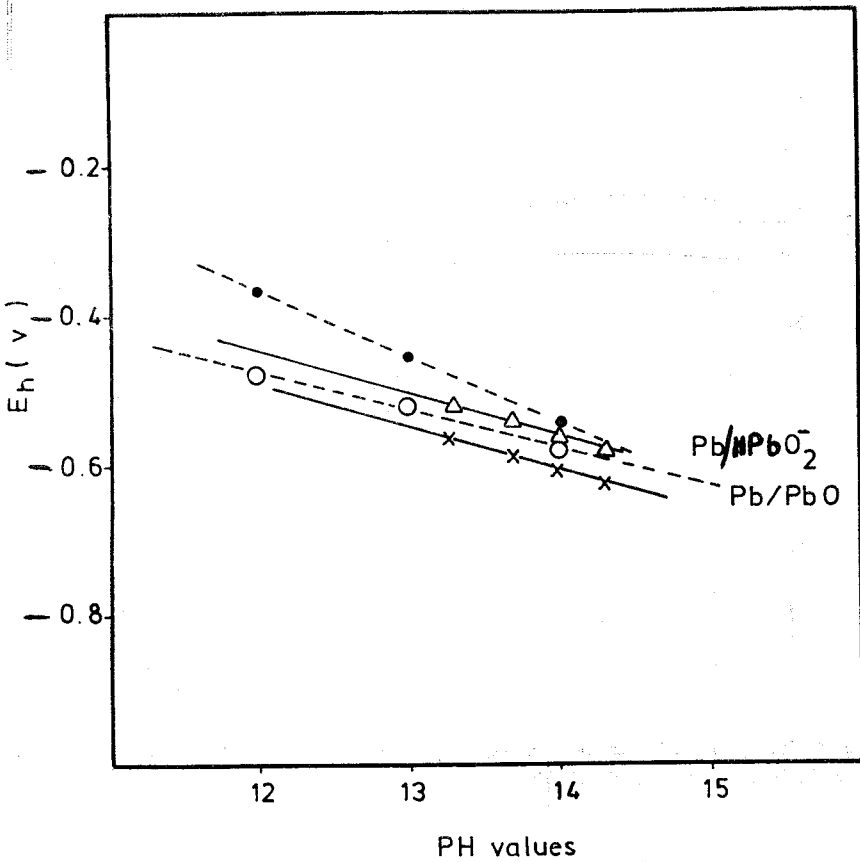
$$Pb + 2\ O\bar{H} = PbO + H_2O + 2e \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$
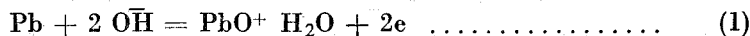
Fig. 1. Effect of pH on the potential of Pb
X pure NaOH
△ 0.5 MoO_4^{-2}

The corrosion rate of the metal, Vcorr, was measured in the pure alkali solutions and the results are given in Fig.(2) It is clear that the metal corrodes, although slightly, in these solutions. One can therefore conclude that the oxide is not quite protective, due most probably, to dissolution in the alkaline solutions forming plumbite according to

$$PbO + O\bar{H} = HPbO_2^- \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (2)$$
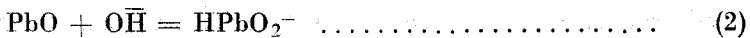
Effect of $M_0O_4^{--}$:

To test the effect of molybdate on the corrosion potential of lead, the potential was measured in (0.2–2M) NaOH, containing (0.0001–
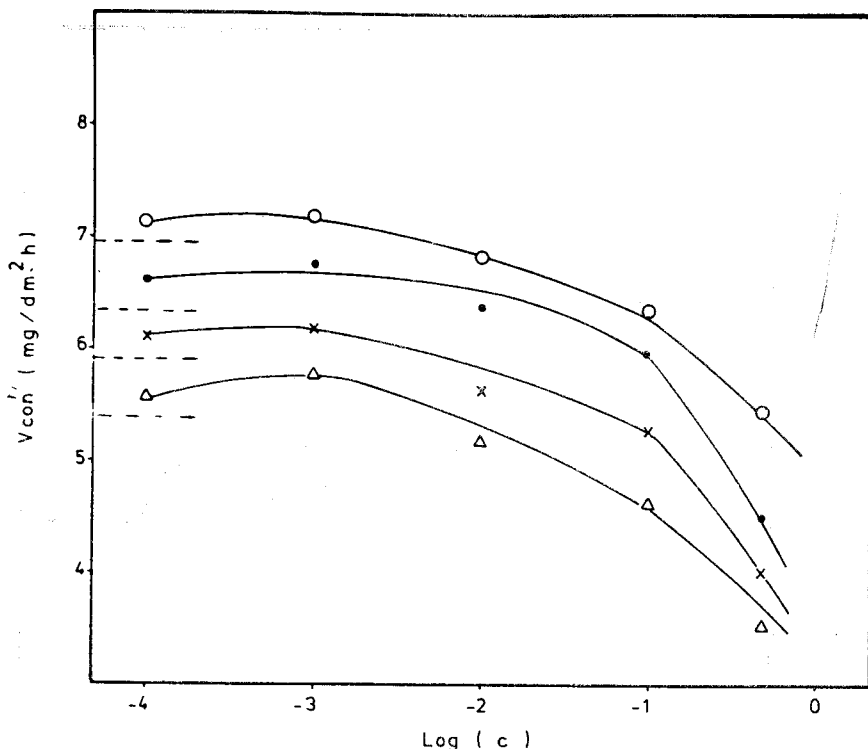
Fig. 2. Rate of corrosion of Lead in Na_2MoO_4 solution containing (02M NaoH, 1M NaoH[2], x 0.5M NaOH and △ 0.2M NaOH).

0.5M) Na_2MoO_4. In Fig. (3), the steady state potentials are plotted as a function of the logarithm of the molar concentration of molybdate, different alkali solutions.

In this figure the steady state potentials in the corresponding free NaOH solutions are represented by dotted lines; these are taken as reference values to those obtained in presence of MoO_4^{-2}. From Fig. (3) it is clear that (except in 2M NaOH) the potential decreases slightly with increase of molybdate concentration.

Corrosion rate measurements were also carried out in the various alkali solutions, containing different molybdate concentrations. The results showed that addition of molybdate is accompanied by decrease in the corrosion rate [c.f. Fig. (2)]. In the light of Evans diagram[5], the decrease of both corrosion potential and corrosion rate indicates that it is the cathodic reaction which is subjectedto deceleration. Such
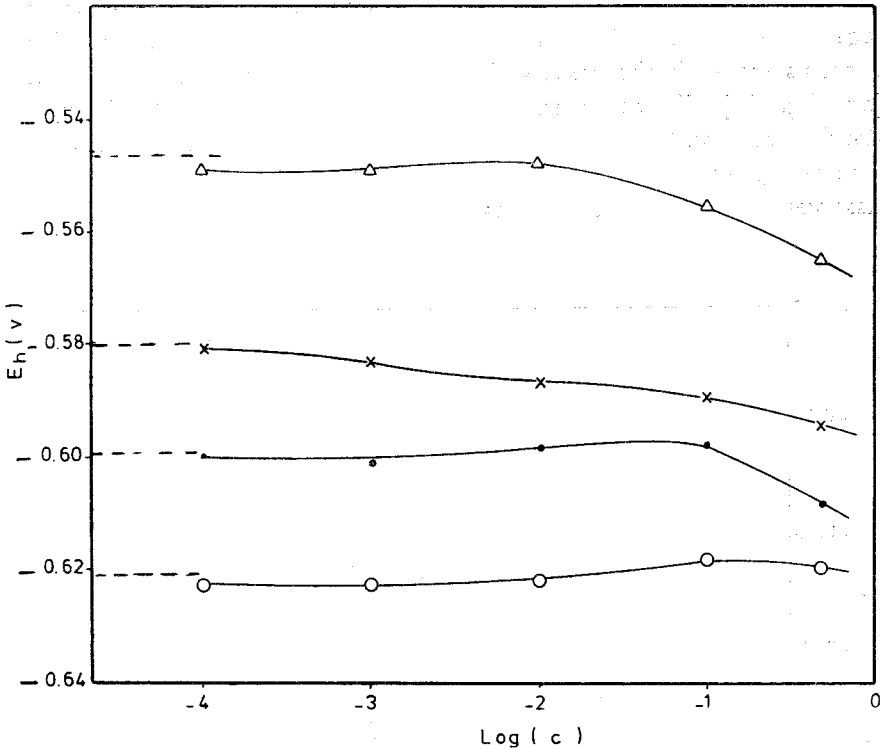
Fig. 3. Effect concentration of Na_2MoO_4 solution containing (02M NaoH, 1M²NaoH, x 0.5M NaOH and △ 0.2M NaOH) on the potential of lead.

inhibiting action might be attributed to adsorption of molybdate ions on the cathodic centers in the oxidefree areas of the surface.

Anodic Polarisation:

In order to throw light on the corrosion behaviour of lead in the molybdate solutions, anodic polarisation measurements were carried out in 0.1M NaOH containing 0.1, 0.01 and 0.001M molybdate. The results are given in Fig. (4). Polarisation was conducted within the current density range 10^{-4}–10^{-1} A / cm².

Generally, the polarisation curves exhibit a region of stationary potential. Which extends up to a certain current density, dependent on the molybdate concentration. The potential then exhibits a linear logarithmic relation, with a slope of about 0.03V. At higher currents, the potential shows rapid increase with the current density indicating the onset of passivity.

As obvious from Fig. (4), the polarisation curve is shifted to more negative potential with increase of the molybdate concentration. This is consistent with the results of measurements of corrosion potential [c.f. Fig. (3)]. The observed Tafel slopes are almost equal to the previously obtained for the anodic dissolution of lead in pure alkali solutions[4]. Those results[4] had been taken to indicate that the metal dissolves in two successive steps as follows:
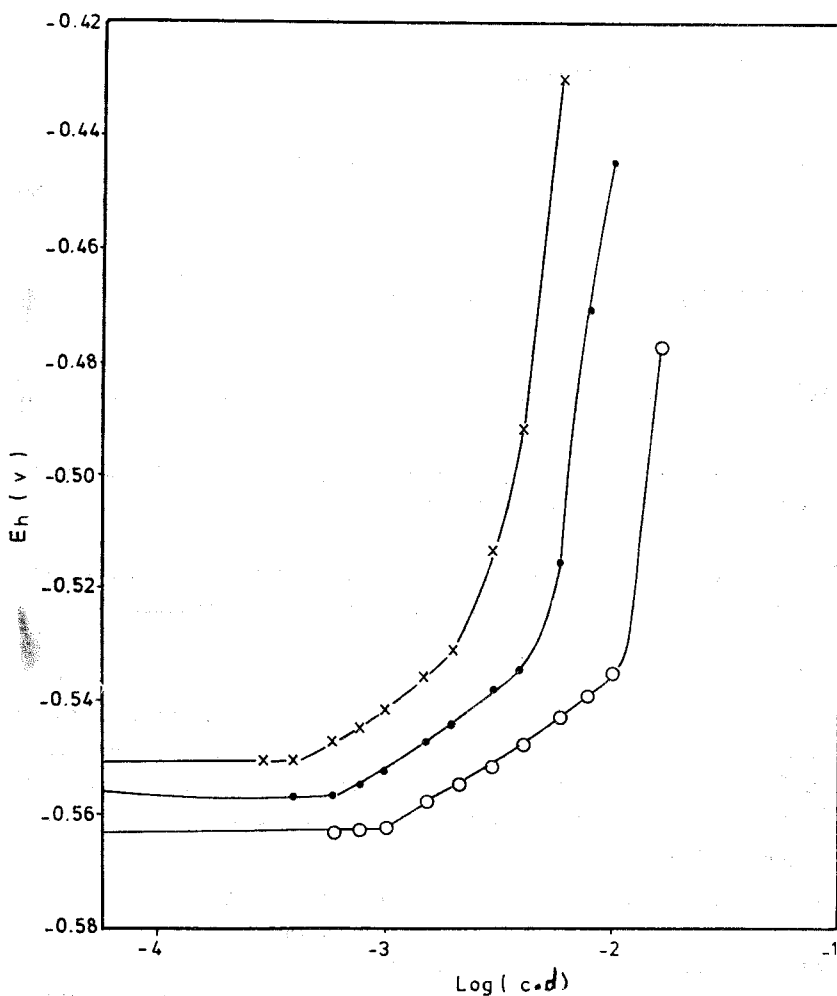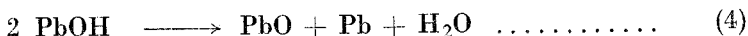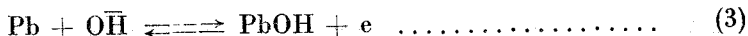

Fig. 4. Anodic polarisation of Pb in 0.1M NaOH containing O 0.1M MoO$_4^{-2}$. 0.01M MoO$_4^{-2}$ x 0.001M MoO$_4^{-2}$.

$$Pb + O\overline{H} \rightleftharpoons PbOH + e \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$2 \; PbOH \quad \longrightarrow \quad PbO + Pb + H_2O \quad \ldots\ldots\ldots\ldots \quad (4)$$

The second reaction is the rete–determining step. The observation of the same Tafel slope in the presence of molybdate, indicates that this ion does not change the mechanism of the anode reaction. However, as evident from Fig. (4), the linear logarithmic part is extended to higher currents as the molybdate concentration is increased; a fact which means that increase of MoO_4^{-2} concentration delays the onset of passivity.

The onset of passivity is usually ascribed to the incomplete removal of the oxide as plumbite.

Hence, the oxide accumulates on the anode surface, leading to rapid increase of potential. Accordinly, one expects that increase of the alkali concentration (at a given molybdate content), delays the onset of passivity. Therefore, potential–current density relations were measured in 0.1, 0.2 and 0.5M NaOH, in presence of 0.5M Na_2MoO_4. As evident from Fig. (5), the current density at which the metal is passivated, increase, although slightly, with increase of the alkali concentration.

Cathodic Polarisation:

Cathodic polarisation measurements were carried out in 0.1M NaOH solution, in presence of 0.001, 0.01 and 0.1M Na_2MoO_4, and the results are shown in Fig. (6). It is evident that the potential remains stationary with a current density range, that increases with increase of the molybdate concentration. Then the potential decreases markedly with the current density. The stationary potential decreases with increase of molybdate concentration, in good agreement with the result of V_{corr} measurements [c.f. Fig. (2)].

The observed stationary potentials in Fig. (4) ranges from −0.563 to −0.570V. These values are markedly less negative than the standard potential for hydrogen evolution from alkaline solution (−0.84V). Hence, the cathodic reaction is not the evolution of hydrogen. It is probable that the molybdate ions are reduced to the pentavalent state. Taking the standard potential in acid solution as 0.4V[7], the potential in alkaline solutions amounts to −0.44V.
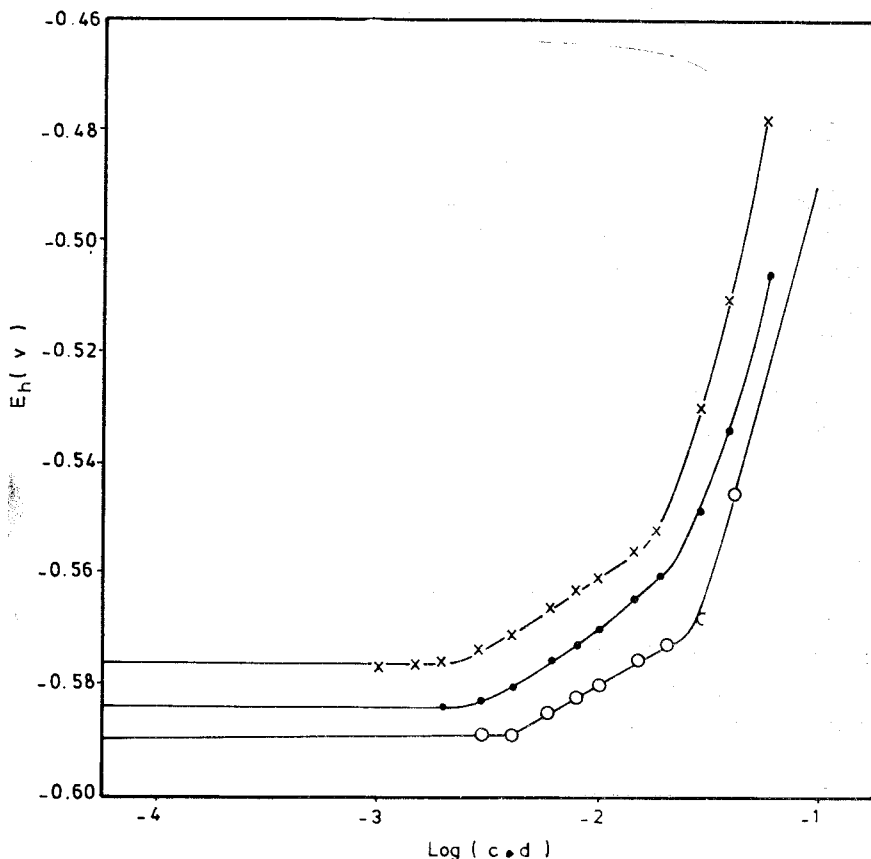
Fig. 5. Anodic Polarisation of Pb in 0.5 MoO_4^{-2} containing.

O 0.5M NaOH

. 0.2M NaOH

x 0.1M NaOH

The observed stationary potential are comparable with this value.

As mentioned above, (and in agreement with the corrosion potential measurements), the increase of molybdate concentration shifts the potential to more negative values. This points out that the cathode becomes less ready to deliver electrons to solution. It seems that the reduction product (containing the pentavalent state), forms with MoO_4^{--} ions a complex anion, which has higher affinity for adsorption on the metal surface. This causes the decrease of the bare cathodic areas. That is why corrosion of the metal is cathodically controlled.
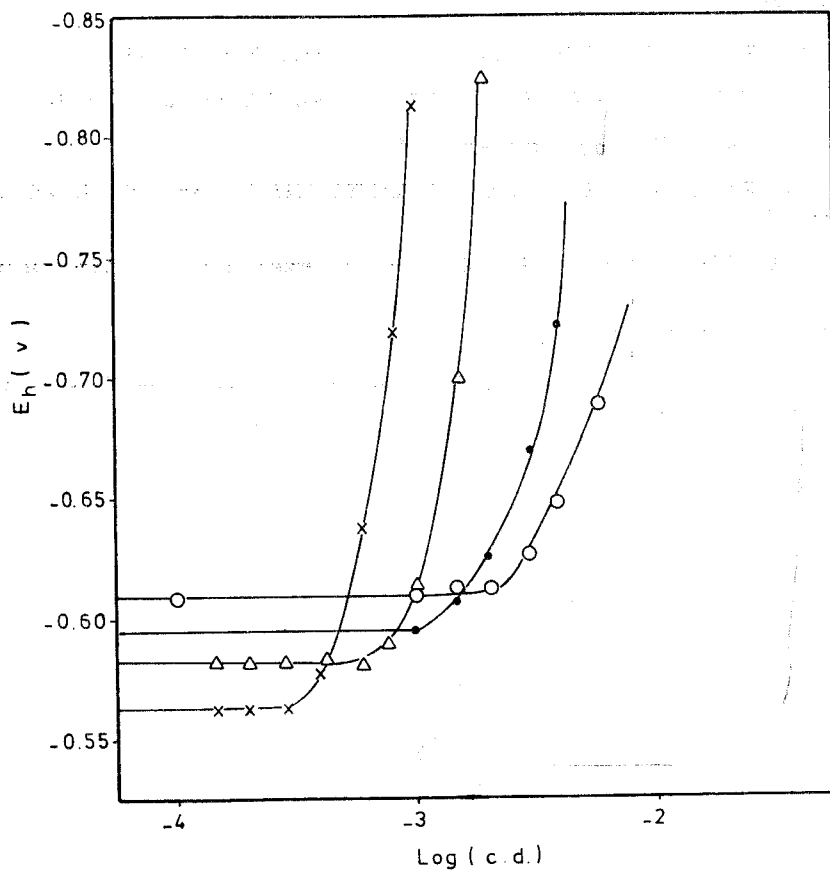
Fig. 6. Cathodic polarisation of Pb in 0.1N NaOH containing:

O 0.5M MoO_4^{-2}
.   0.1M MoO_4^{-2}
x   0.001M MoO_4^{-2}

Accordingly to this argument, the passivation current, at a given molybdate concentration, should increase as the alkali concentration is increased. This is actually true as evident from Fig. (5) which shows polarisation curves in 0.1, 0.2 and 0.5 5M NaOH solutions containing 0.5M molybdate.

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