Anodic behaviour and passivation of a lead electrode in sodium carbonate solutions

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Cyclic voltammograms of a lead electrode were obtained in Na₂CO₃ solution as a function of the starting potential, electrolyte concentration and voltage scanning rate. The shape of the voltammograms was found to depend on the starting potential as well as the sweep number. This is probably due to changes in the activation state of the electrode surface. The first anodic portion of the voltammograms is characterized by a shoulder and two peaks corresponding to the formation of PbCO₃, PbO and PbO₂, respectively. The cathodic portion shows the occurrence of two peaks corresponding to the reduction of PbO₂ to PbO and PbO to Pb, successively, followed by the formation of PbH₂. An increase in concentration of CO₃²⁻ ions leads to a negative shift in the values of the peak potentials, $E_p$, accompanying the formation of PbO and PbO₂. In addition, the current density for both the anodic oxidation peaks showed marked dependence on the concentration of the electrolyte. An increase in the scanning rate was observed to lead an increase in the size of the voltammograms. The current density of both the anodic peaks and the anodic passivation region were proportional to $v^{1/2}$. Such behaviour is expected in a diffusion-controlled processes. In addition, the anodic peaks are shifted towards more positive values of potential, whereas the cathodic peaks are shifted in the negative direction, indicating irreversible formation of the passive film on the electrode surface.

1. Introduction
The electrochemical behaviour of lead in carbonate media has attracted attention because the major part of the early work was performed galvanostatically and the results were poorly resolved [1, 2]. To date no information has been reported in the literature regarding the interpretation of the cyclic voltammograms (CVs) of lead in carbonate media.

The present paper is concerned with the study of the electrochemical behaviour of lead in Na₂CO₃ solution employing the cyclic voltammetric technique. The influence of starting potential, carbonate concentration, and scanning rate were examined. The implications of these results with reference to the mechanisms of the reaction involved, is discussed.

2. Experimental procedure
Spectroscopically pure lead (Johnson-Matthey, UK) was used as the test material throughout the present work in the form of short rods, 0.98 mm diameter. These rods were fixed to Pyrex glass tubes with Araldite so that the total exposed surface area was 0.75 cm². Electrical contact was achieved through thick copper wires soldered to the end of the rods, not exposed to the solution. Before being used, the electrodes were abraded, successively, with 0-, 00- and 000-grade emery papers, then degreased with acetone and finally washed with doubly-distilled water (which was also used in preparing the electrolytes of Na₂CO₃).

A two-compartment cell was used for obtaining the CVs. The counter electrode was a platinum wire. Its compartment was separated from the working electrode (main) compartment by means of a G₄ centred glass disc. The potential of the working electrode was measured relative to a saturated calomel electrode (SCE) using a salt bridge, whose tip was almost touching the electrode surface.

The potential of the working electrode was controlled by a Wenking laboratory Potentiostat (LB75). A voltage scan generator (VSG72, Wenking) was used to provide a linearly increasing or decreasing control voltage input to the potentiostat. The CVs were recorded using an X–Y recorder-type Linseis LY.21 (Cole Parmer Instruments, USA). Each experiment

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was performed on a newly polished electrode and with freshly prepared electrolyte. The temperature was adjusted to 25 ± 0.2 °C using an air thermostat.

3. Results and discussion

3.1. Effect of starting potential

Fig. 1 shows the curves of three different CVs starting from the quasi-steady state potential (\(E = -0.7\) V SCE), in \(1 \times 10^{-1}\) mol l\(^{-1}\) Na\(_2\)CO\(_3\) solution at a sweep rate 25 mV s\(^{-1}\). The first curve represents the first sweep, the second and third sweeps are also illustrated. It is obvious that the forward and backward sweeps are different. This could be an indication of an irreversible process. Dissimilarities between successive sweeps can be attributed to different initial states of the electrode surface. After the first sweep, the electrode surface is thought to be covered partially by the oxidation products that have not been reduced. Therefore, the second and third sweeps are quite different, as would be expected. The initial state of the electrode determines, to a large extent, the shape of the resulting CVs, as can be seen by inspection of the curves of Figs 2–4. In these figures, the electrode was polarized cathodically at -1.2, -1.6 and -2.1 V, respectively, for 10 min before starting the CVs. In all cases, the behaviour demonstrated by the CVs is quite different from that in Fig. 1.

The results of Figs 1–4, are a clear indication that the initial state of the electrode surface seems to be an important factor regarding the shape of the current–potential curves. The interesting point here is that if polarization started at the open-circuit potential (-0.7 V (SCE)), the electrode might have been covered with a pre-immersion oxide film, Fig. 1. This would possibly arise from atmospheric oxidation of the metal surface or from corrosion taking place at the designated open-circuit potential [3]. Undoubtedly, the resulting CVs will be a function of these different starting conditions. However, Fig. 4 illustrates that hydrogen evolution ensues at a starting potential of -2.1 V (SCE). In this case, the oxide film on the electrode surface can be reduced [4], and a reproducible initial state of the electrode surface is consequently achieved. Thus, comparison of the different results requires prior knowledge of the starting conditions [3, 5–7].

Figure 1 Scanning voltammograms of the lead electrode in \(1 \times 10^{-1}\) mol l\(^{-1}\) Na\(_2\)CO\(_3\) starting from the open-circuit potential, -0.7 V (SCE), at a rate of 25 mV s\(^{-1}\). Sweep: (—) 1, (. . . .) 2, (—) 3.