Corrosion and passivation of Pb in CO$_2^-$ solutions

S S El-Egamy & W A Badawy*
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt
Received 31 May 1994; accepted 22 February 1995

The electrochemical behaviour of lead in carbonate solutions has been investigated using impedance, cyclic voltammetry and open-circuit potential measurements. Under open-circuit conditions, the lead electrode has been passivated by the formation of PbCO$_3$ film. The rate of passivation is found to be dependent on the carbonate ion concentration. The reciprocal capacitance, the polarization resistance and the equilibrium electrode potential are found to increase with time following a simple logarithmic law. Cyclic voltammograms of Pb in 0.15 M Na$_2$CO$_3$ display three anodic current peaks. The peaks correspond to the oxidation of Pb into PbCO$_3$, the transformation of PbCO$_3$ into PbO, and then the further oxidation of PbO into PbO$_2$. On reversing the scan, two reduction peaks could be observed. The first is due to the reduction of PbO$_2$ into PbO and the second corresponds to the transformation of PbO into PbCO$_3$. The peak currents are found to be dependent on both the sweep rate and electrolyte concentration. The non-linear dependence of the peak current on the sweep rate indicates that the passivation process is irreversible and controlled by several factors other than diffusion of Pb$^{2+}$ ions.

The electrochemical behaviour of lead in acid solutions was extensively studied$^1-^5$. Little attention has, however, been paid to the behaviour of the metal in alkaline solutions$^6-^9$. The work done in this area has focused primarily on Pb dissolution reactions and utilized only steady-state approaches. Preliminary work on film formation on the lead electrodes has indicated that both PbO and PbO$_2$ films form on the electrode surface$^7,8$. PbO was assumed to be the primary film product$^8$. Recently, the reactions of lead in sodium carbonate solutions were investigated using galvanostatic polarization technique$^9$. In solutions with concentrations varying between 0.05 and 0.3 M Na$_2$CO$_3$, three arrests were observed. These arrests correspond to the oxidation of Pb to PbCO$_3$, which transforms to PbO and the later to PbO$_2$, before oxygen evolution. In concentrated Na$_2$CO$_3$ solutions (> 0.3 M), the first and last arrests were only recognized. Passivation of Pb in Na$_2$CO$_3$ solutions covering the range of concentration 0.05-0.5 M was presented by the relation:

$$\log t = A - n \log i$$

where $i$ is the current density and $t$ is the time elapsed before oxygen evolution$^9$. The behaviour of Pb in carbonate solutions seems to be very important. The importance of the study of the corrosion and passivation of lead in carbonate solutions is coming from the use of lead in the disposal of high-level nuclear waste buried below the surface of a stable rock formation and the suitability of carbonates in complexing UO$_3^+$ with the dissolution of UO$_2$$^{10}$. Besides acting as a corrosion barrier the use of lead has many advantages. It could act as a redox scavenger by removing dissolved oxidants from ground water and slowing down the oxidative dissolution of the UO$_2$ fuel. The metal (Pb) forms sparingly soluble basic lead compounds with a number of anions in the ground water$^{11}$. This is of particular advantage in the case of carbonate that strongly complexes UO$_3^+$ with the dissolution of UO$_2$ as UO$_2$(CO$_3$)$_{3/2}^-$ and UO$_2$(CO$_3$)$_{4/2}^-$. The interaction of Pb or PbO with carbonate solutions may lead to the formation of solid films on the electrode surface which are very useful in preventing access of ground water to the waste form and impeding the subsequent release of radionuclides$^{12}$. The aim of the present investigation is to throw some more light on the electrochemical behaviour of Pb in sodium carbonate solutions taking into account the various phases which might form on the metal surface. In this respect, cyclic voltammetry (CV), potentiodynamic, open-circuit potential and electrochemical impedance spectroscopy (EIS) were used.

*Author to whom all correspondence should be addressed.
Present address—Department of Chemistry, Faculty of Science, University of Kuwait, P B 5969, 13060 Safat, Kuwait.
Experimental Procedure

The working electrode was made as a disc of massive, spectroscopically pure lead (Aldrich-Chemie) of area 0.237 cm$^2$. Electrode preparation and electrochemical cell were as described elsewhere$^{13}$. Before each experiment, the electrode surface was pretreated in a reproducible manner by mechanical polishing with various grades of emery papers (up to 1000 grid) under a stream of distilled water. The electrode is then dried and rubbed against a smooth cloth, then finally rinsed in acetone and distilled water in an ultrasonic bath. The final step is the electrochemical cleaning of the electrode by cathodic polarization at $-1.2$, V (vs SCE) for 5 min in the test solution. The electrochemical cell is a double walled three electrode cell. The reference electrode was a saturated calomel electrode (SCE) and a spiral platinum wire was used as a counter electrode.

The electrode impedance was measured using IM5d-AMOS-System (Zahner Elektrik GmbH & Co., KRONACH, Germany). A 10 mV amplitude signal and a frequency range of $0.1-1 \times 10^5$ Hz were normally used. Potential sweep (CV) measurements were carried out using a fast response potentiostat in conjunction with a linear sweep generator. All solutions were prepared using analytical grade reagents (PA) and triply distilled water. The experimental temperature was adjusted at $25 \pm 0.1 ^\circ C$ using an electronic water thermostat.

Results and Discussion

Open-circuit potential measurements—The open-circuit potential, $E$, the cell impedance, $Z$, and the phase shift, $\theta$, were measured with time in sodium carbonate solutions of different concentration. The data were presented in Fig. 1 (a, b and c). The open-circuit potential drifts continuously toward nobler values (Fig. 1a). This behaviour denotes that the pre-immersion film present on the surface of the metal is too thin to impart complete passivity$^{14}$. Healing and further thickening of that film by formation of a thin lead carbonate layer may occur until a steady state is achieved. Film formation progress on the expense of anodic active centers and hence the anodic process gets more polarized. The potential increased with time following a simple logarithmic
The polarization resistance, \( R_p \), which is of practical importance in determination of instantaneous corrosion rate, can be obtained from the values of the real part of admittance at the lowest frequency \( \omega_0 \). It can be also obtained from the Bode diagram by estimating the values of the impedance at very low frequency (0.1 Hz).

The values of \( C_d \) and \( R_p \) for the lead electrode in carbonate solutions were evaluated at different time intervals. Fig. 1c presents the variation of \( R_p \) with \( \log t \). The relation is a straight line with an intersection. Plots of \( C_d^{-1} \) vs \( \log t \) are similar, i.e., two straight line segments are present. These data can be represented by the following equations:

\[
R_p = \alpha' + B' \log(t + t_o) \quad \ldots \text{(4)}
\]

\[
C_d = \alpha'' + B'' \log(t + t_o) \quad \ldots \text{(5)}
\]

where \( B' \) and \( B'' \) are the rate coefficients of film thickening. The rate coefficients corresponding to the two segments of the straight lines in different carbonate concentrations are presented in Table 1. According to the values of \( B'_1 \) and \( B'_2 \), the rate of film thickening increases as the carbonate concentration increases which indicates that the lead electrode passivates with increasing carbonate concentration.

The polarization resistance, \( R_p \), which is of practical importance in determination of instantaneous corrosion rate, can be obtained from the values of the real part of admittance at the lowest frequency \( \omega_0 \). It can be also obtained from the Bode diagram by estimating the values of the impedance at very low frequency (0.1 Hz).

The values of \( C_d \) and \( R_p \) for the lead electrode in carbonate solutions were evaluated at different time intervals. Fig. 1c presents the variation of \( R_p \) with \( \log t \). The relation is a straight line with an intersection. Plots of \( C_d^{-1} \) vs \( \log t \) are similar, i.e.,

\[
E = \alpha + B \log(t + t_o) \quad \ldots \text{(2)}
\]

where \( \alpha \) and \( B \) are constants. \( B \) represents the rate coefficient of the film formation process. The \( E \) vs \( \log t \) relation consists of two linear segments of different slopes \( B_1 \) and \( B_2 \) (cf. Fig. 1a): This indicates that the rate of film thickening changes with time from \( B_1 \) to \( B_2 \) corresponding to the first and second segments of the \( E \) vs \( \log t \) relation, respectively. In very dilute solutions (\( \leq 0.025 \ M \) Na\(_2\)CO\(_3\)), the slope of the second segment, \( B_2 \), is about zero, which means that a steady state occurs after a 3 min of electrode immersion in these solutions. In this case, the rate of passive film thickening is equal to the rate of its dissolution.

Impedance measurements—Electrochemical impedance spectroscopy (EIS) has been successfully used in kinetic studies and corrosion phenomena especially for polymer coated metals, anodized metals and passivated alloys\(^{15,16} \). It has been recently used to detect pitting corrosion\(^{17,18} \).

Electrode impedance measurements provide strong support for any changes in the film thickness\(^{14} \). Fig. 1b presents typical Bode diagrams at different time intervals for the Pb electrode in 0.15 M Na\(_2\)CO\(_3\). The data represent simple impedance behaviour including one capacitive component without any sign of diffusion. The electrochemical system in this case can be represented by the Randels equivalent circuit which has been applied to a corroding metal/solution interface\(^{19} \).

The double layer capacitance, \( C_d \), can be obtained from the value of \( Z \) at the intermediate frequencies where the impedance data give a straight line with a slope of \( \approx -1 \). It can be also obtained from the value of the imaginary part \( (Z_{im}) \) at the same frequency using the relation:

\[
C_d = \frac{1}{2\pi f_{\omega_{\text{max}}} \cdot Z_{\omega_{\text{max}}}} \quad \ldots \text{(3)}
\]

The polarization resistance, \( R_p \), which is of practical importance in determination of instantaneous corrosion rate, can be obtained from the values of the real part of admittance at the lowest frequency\(^{20} \). It can be also obtained from the Bode diagram by estimating the values of the impedance at very low frequency (0.1 Hz).

The values of \( C_d \) and \( R_p \) for the lead electrode in carbonate solutions were evaluated at different time intervals. Fig. 1c presents the variation of \( R_p \) with \( \log t \). The relation is a straight line with an intersection. Plots of \( C_d^{-1} \) vs \( \log t \) are similar, i.e.,

Cyclic voltammetry measurements—In this series of experiments, the mechanically polished lead electrode was cathodically polarized at \( -1.2 \) V for 5 min in carbonate solutions of different concentration. Potentiodynamic runs were carried out at a sweep rate of 10 mV s\(^{-1} \). Typical voltammograms of the lead electrode in Na\(_2\)CO\(_3\) solutions of different concentrations are presented in Fig. 2a. On the anodic scan, three current peaks can be observed, which correspond to the oxidation of lead into PbCO\(_3\), than into PbO. The latter oxidizes to \( \alpha\)-PbO\(_2\) then followed by oxygen evolution. On the reverse scan, two reduction peaks only could be obtained. The first corresponds to the reduction of \( \alpha\)-PbO\(_2\) to PbO and the second corresponds to the formation of PbCO\(_3\). The mechanism controlling the reactions occurring at the electrode surface may be represented by:

\[
Pb + CO_3^{2-} \rightarrow PbCO_3 + 2e^-
\]

\[
PbCO_3 + H_2O \rightarrow PbO + H_2CO_3
\]

\[
PbO + 2OH^- \rightarrow PbO_2 + H_2O + 2e^- \quad \ldots \text{(6)}
\]

\[
PbO_2 + Pb \rightarrow 2PbO
\]

\[
PbO + CO_3^{2-} + H_2O \rightarrow PbCO_3 + 2OH^-
\]

As the carbonate concentration increases, the oxidation rate increases with the formation of insoluble lead carbonate deposit, which on further anodization undergoes further oxidation to PbO.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( B'_1 )</th>
<th>( B'_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 M</td>
<td>2.45</td>
<td>15</td>
</tr>
<tr>
<td>0.15 M</td>
<td>3.08</td>
<td>15.5</td>
</tr>
<tr>
<td>0.05 M</td>
<td>3.17</td>
<td>17.5</td>
</tr>
<tr>
<td>0.025 M</td>
<td>3.50</td>
<td>19.0</td>
</tr>
</tbody>
</table>
and then to PbO₂. The effect of carbonate concentration on the peak currents is presented in Fig. 2b. The peak current of the second anodic peak (Iₚ₂) increases as the carbonate concentration increases. The relation was found to be not linear as it was expected by Delehay²⁰. The same phenomenon was observed with the other peak currents which may indicate that the reactions leading to insoluble products are irreversible reactions.

The effect of the sweep rate on the cyclic voltammograms of the lead electrode in the carbonate solutions was also investigated. Typical voltammograms of Pb in 0.15 M Na₂CO₃ at different sweep rates are shown in Fig. 3a. The different peaks are affected differently by the scan rate. By increasing the scan rate, the more positive peak becomes ill defined. Better resolution between the more positive peak and the oxygen evolution wave can be obtained only with sweep rates less than 20 mVs⁻¹. The relation between the peak currents and the sweep rate v cannot be represented by the simple equation:

\[ I_p = K v^n \]  

where \( I_p \) is the peak current, \( K \) is constant and \( n \) is the power to which the sweep rate, \( v \), is raised. A plot of \( \log I_p \) vs \( \log v \) will yield a straight line with a slope of unity for the region where the peak current is linear with the scan rate, i.e., the region in which thin film formation is expected²¹. For the lead electrode in carbonate no thin film
Fig. 3a—Cyclovoltammograms of Pb in 0.15 M Na₂CO₃ solution at different scan rates [(1) 2 mV s⁻¹, (2) 5 mV s⁻¹, (3) 10 mV s⁻¹, (4) 20 mV s⁻¹ and (5) 40 mV s⁻¹].

Fig. 3b—$I_p$ vs $v^{1/2}$ relation for the lead electrode in 0.15 M Na₂CO₃ solution.

formation behaviour alone could be obtained. A plot of $I_p$ vs $v^{1/2}$ give straight line of two slopes with a deviation from the perfect linear behaviour expected for reactions controlled by simple diffusion. This indicates that the behaviour of the lead electrode in the carbonate solution is controlled by a complex mechanism and not by a simple diffusion process. The shift of the peak potential with the change in the sweep rate is an indication of irreversibility and complexity of that behaviour.

The results of cyclic voltammetry together with EIS represent strong evidence that the passivation of Pb in CO₃⁻ solutions cannot be represented by a simple diffusion controlled mechanism as was given earlier. In order to correlate the constant potential corrosion data with the results of cyclic voltammetry, the potential of the lead electrode was held constant at +1.4 V (vs. SCE), for 3 h and then reduced potentiodynamically to -1.2 V at a sweep rate of 2 mV s⁻¹. Fig. 4 shows the current-bias potential characteristics of the anodically formed deposit. Two cathodic peaks are present at +0.156 and -0.977 V corresponding to the reduction of the PbO₂ deposit to PbO and then to PbCO₃.

Although cyclic voltammetry is very sensitive to changes in the kinetics of the electrode processes, it has the disadvantage of covering a large voltage range. A variety of products can be formed making it difficult to isolate the reaction of interest. To overcome this difficulty, the lead electrode was subjected to corrosion at constant potential of 1.4 V in 0.15 M Na₂CO₃ solution. After the electrode had corroded, the potentiostat was disconnected, and the electrode was allowed to self discharge in the same solution. The open-circuit potential was monitored as a function of time. The voltage decay curves of the passivated lead electrode are presented in Fig. 4b. In the voltage
decay process two plateaux were observed at +0.2 and −0.58 V, corresponding to reduction of PbO₂ to PbO and then to PbCO₃.

Oxidation of Pb to PbCO₃—In this part the kinetics of PbCO₃ formation on the lead electrode surface will be investigated. The lead electrode was passivated at constant potential of −0.5 V (vs SCE) in 0.15 M Na₂CO₃ solution. The cell impedance and the phase shift were measured at different time intervals during the potentiostatic anodization process. Fig. 5a shows the Bode plot representing the behaviour of the Pb-electrode in the sodium carbonate solution. The electrode impedance increases with time indicating passivation of Pb by the formation of PbCO₃ deposits. The data are similar to those presented in Fig. 1b, i.e., representing simple impedance behaviour that can be modeled by the Randels equivalent circuit 19. The double layer capacitance (Cₐ) and polarization resistance were obtained as described earlier. The variation of the reciprocal capacitance (Cₐ⁻¹) with the logarithm of time is linear indicating that the film formation process obeys Eq. (5) (cf. Fig. 5b). The increase of Rₚ with increasing time intervals indicates the passivation of the lead electrode in the carbonate solution (cf. Fig. 5a).
Conclusion

The passivation of lead in carbonate solutions cannot be represented by a diffusion controlled mechanism. It should be represented by a complex mechanism taking into consideration the formation of PbCO$_3$ deposit rather than the thin film formation and the irreversibility of the process which is clear in the cyclic voltammetry measurements. The lead carbonate deposit inhibits the further corrosion of lead and prevents the access of ground water to the nuclear waste and impedes the subsequent release of radionuclides from the high level nuclear waste.

References