

ELECTROCHEMICAL PHASE FORMATION ON UNDERPOTENTIAL AND OVERPOTENTIAL DEPOSITION OF LEAD ON GLASSY CARBON

S JAYA, T PRASADA RAO and G PRABHAKARA RAO
Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

The electrocrystallisation of lead on GCE in underpotential and overpotential regions, is described. The monolayer stripping peak occurring with large underpotential shift does not correlate with the difference in chemical potential values of lead and carbon. The analysis of the stripping peak revealed that the monolayer is formed by electrocrystallisation. The nature of overpotential deposition is independent of the presence or absence of UPD lead and is dependent mainly on the concentration of lead in solution and on the nature of substrate.

Key Words: Electrochemical phase formation, under and overpotential deposition, Lead on glassy carbon.

INTRODUCTION

The phenomenon of underpotential deposition (UPD), the deposition of first layer or monolayer of metal atoms onto a foreign metal substrate at more positive potential to the bulk deposition potentials, is quite well known [1, 2]. The presence of UPD peaks during the electrochemical phase formation (ECPF) of copper and mercury on glassy carbon has been reported by us earlier [3, 4]. A generalized correlation between the difference in deposition potentials of the monolayer and bulk (ΔU_p) with another physical quantity characteristic of the system viz the difference in work functions of the substrate and depositing metal ($\Delta \Phi$), viz $\Delta U_p = 0.50 \Delta \Phi$, based on studies over a wide range of $\Delta \Phi$ for twenty one pairs of metals is available [5]. However, a later report [6] could not explain: (i) the occurrence of UPD peaks in lithium, mercury and lead or (ii) its absence in the case of cadmium, silver, tin and copper, on pyrolytic graphite. This led to the suggestion that the occurrence of UPD metal on graphitic should not only depend on the work functions but also on the activation energy of dehydration for a particular ion [6]. During the course of our studies on the ECPF of lead on GCE we noticed the presence of monolayer stripping peak at a potential which is far more positive to the bulk stripping peak as compared with the expectation based on the above correlation [5]. This paper reports the details of these results together with the characterization of UPD peak and its influence on the overpotential deposition of lead.

EXPERIMENTAL

The working electrode was a polycrystalline GCE, 0.0707 cm² geometric area. The electrode surface was polished with emery papers of increasing fineness (1/0 to 4/0). A bright platinum foil counter electrode and a normal calomel reference electrode were employed in a three-electrode cell assembly. A potentiostat, a potential scan generator, and digigraphic X-Y Recorder were used. All the solutions were prepared using AR grade reagents in conductivity water. Studies were carried out using various concentrations of lead in 1M potassium nitrate solutions.

RESULTS AND DISCUSSION

Underpotential deposition of lead on GCE

Fig. 1 shows the cyclic voltammogram of 0.01 M lead solutions in 1 M

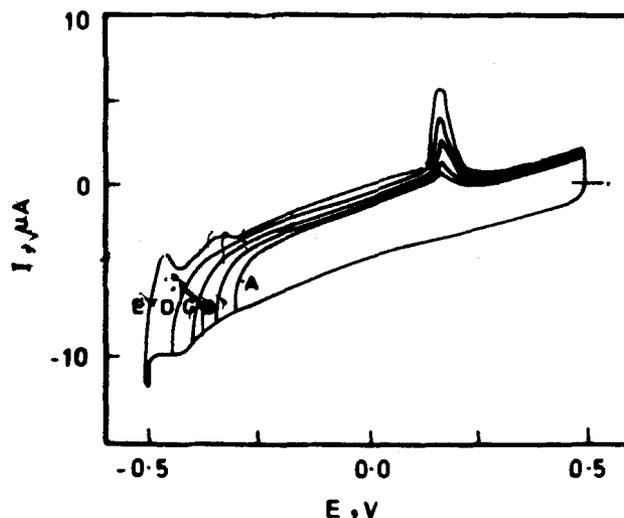


Fig. 1: Cyclic voltammetric I-E curves obtained for a solution containing 0.01 M of $Pb(NO_3)_2$ in 1M KNO_3 on GCE at a scan rate of 100 mV/s. Lower limit of potential sweep is -0.3, -0.35, -0.40, -0.45 and -0.50 V vs NCE for curves A to E respectively.

potassium nitrate solutions on glassy carbon. When the cathodic limit of the cyclic voltammogram is restricted to -0.3 V a stripping peak appears at 0.16 V with a peak width at half height ($\Delta \eta_{1/2}$) of 10 mV. This peak occurring at a far more anodic potential with respect to bulk stripping peak was identified to be due to the stripping of underpotentially deposited lead as such peak is absent in the cyclic voltammogram of GCE in 1 M KNO_3 solution free from lead ions. On increasing the cathodic limit of the cyclic voltammogram from -0.3 to -0.45 V in steps of 0.05 V, the height of the stripping peak increases. On increasing the cathodic limit further to -0.5 V additional features in the stripping curve occur as follows. A prominent peak at -0.48 V and a peak at -0.35 V with not so prominent characteristics are noted. It can be inferred from the above that the stripping peak occurring at -0.48 V is to the stripping of lead deposited in the bulk region.

By taking the chemical potential values of polycrystalline carbon and lead as 5.0 and 4.18 respectively [7], a monolayer stripping peak is expected to appear at 0.41 V more positive to the bulk stripping potential of lead [5]. The presence of a prominent UPD peak at 0.16 V with an underpotential shift as high as 0.64 V cannot be explained by the correlation referred to above [5]. However, the occurrence of very sharp monolayer peaks with large potential shifts (ΔU_p) are known in UPD studies on thallium on to silver single crystal surfaces [8]. These have been attributed to the electrocrystallization of thallium during monolayer formation. It is known that the half-width of monolayer peak ($\Delta \eta_{1/2}$) increases with increasing underpotential shift (ΔU_p), the values of $\Delta \eta_{1/2}$ for $\Delta U_p \rightarrow 0$ being around 90-120 mV [2] for a one-electron transfer as per Langmuir's adsorption. The attraction or repulsion among adatoms results in either sharpening or broadening of the monolayer peaks (i.e. Frumkin's type adsorption). However, the attraction among adatoms cannot explain the $\Delta \eta_{1/2}$ value as low as 5 mV observed in the present study. These earlier reports qualitatively rule out the possibility of adsorption processes being responsible for the monolayer formation of lead. The prominent UPD peak occurring at 0.16 V (Fig. 1) was characterized as due to electrocrystallization using the theoretical criteria laid down recently [9]. The features of the other peak occurring at -0.35 V were not prominent to analyse it under any experimental conditions and is possibly associated with monolayer.

Apart from the occurrence of sharp monolayer peaks, $\Delta \eta_{1/2}$ changes from 5 to 30 mV on increasing the sweep rate from 0.67 to 100 mV/s, thereby suggesting that the formation of monolayer through nucleation growth process (in contrast to a change of $\Delta \eta_{1/2}$ from 44 to 60 mV on increasing the sweep rate from zero to ∞ assuming $n = 2$ expected for an adsorption process). To characterize further the nucleation process as instantaneous or progressive, we proceed as follows:

The formation of monolayer by instantaneous nucleation and growth mode is ruled out from (i) the failure to comply with the global test viz. plot of $\text{Coth } E_p$ vs I_p being non-linear and (ii) the absence of linearity of I_p vs E_p^{-1} plot.

On the other hand, the plot of I_p vs E_p^{-2} gave a linear plot (Fig. 2) indicating that monolayer formation of lead occurs by progressive nucleation-growth mechanism. This is further confirmed from the observed

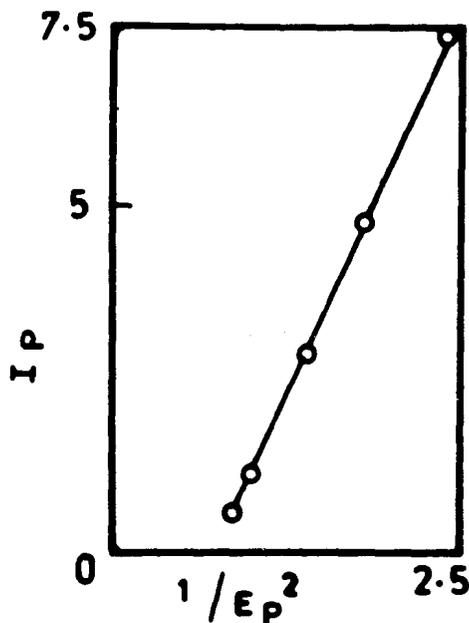


Fig. 2: Plot of I_p vs E_p^{-2} for the UPD lead on GCE (I_p and E_p are non-dimensional quantities)

linear relationship between E_p and $\ln V$ (Fig. 3). From the measured slope of the linear plot in Fig. 2 and the intercept in Fig. 3, the respective kinetic parameters viz. activation parameter (α) and nucleation-growth rate constant (β_0) were calculated and found to be 56 and $10^{3.34}$ respectively. The anodic charge transfer coefficient (α_a) was calculated to be 0.5 from the value of $\Delta \eta_{1/2}$ at higher sweep rates assuming $n = 2$ [9].

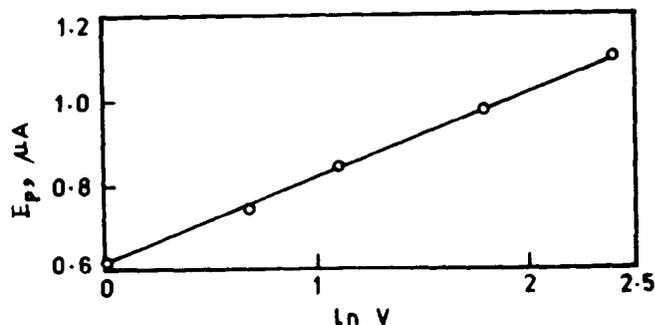


Fig. 3: Plot of E_p vs $\ln V$ for the UPD lead on GCE

Overpotential deposition studies of lead on GCE

The overpotential deposition (OPD) of 0.1 M lead on GCE was shown to follow 3D nucleation and subsequent crystal growth by subjecting to the triangular scans of potential [10]. The onset of nucleation in forward scan triggers current maximum on scan reversal which is characteristic of 3D nucleation and distinguishes it from charge transfer, diffusion control and adsorption kinetics. Recently we have shown that the occurrence of current maximum on scan reversal depends on the nucleation parameter and growth rate constant which are in turn dependent on the nature of the GCE surface and concentration of depositing metal [3]. Further, it was also shown that the appearance of cross-over loop is a sufficient enough condition to distinguish 3D nucleation-growth kinetic processes from other processes. Detailed investigations carried out on the effect of concentration, cathodic potential limit of the triangular scan and sweep rate on the OPD of lead yielded additional information on the system as described below.

By subjecting to triangular scans of potential and restricting the cathodic limit of the scan to different values in the initial stages of crystallization, the various cyclic voltammograms obtained are shown in Fig. 4. When the cathodic potential is limited to -0.491 V the normal cyclic voltammogram without any cross-over is obtained. However, on changing the cathodic limit of the triangular scan to -0.492 V or above a sudden increase in current was observed on forward scan due to the onset of nucleation as evidenced by a current maximum after scan reversal. The cross-over potential remains constant as seen from cyclic voltammograms B, C and D indicating that interfacial controlled 3D nucleation-growth kinetics as operative. Fig. 5 shows the effect of sweep rate on OPD of 0.1 M lead in 1M KNO_3 on GCE. It is clear from figure that, for sweep rates in the range 6 to 11 mV/s, a characteristic cross-over loop is seen with a current maximum on scan reversal. On the other hand, increase of sweep rate to 30 and 50 mV/s results in disappearance of bulk deposition peaks. However, even in these sweep rates, by changing the cathodic limit of the triangular scan to more negative potentials (not shown in Fig. 5) one can notice occurrence of such cross-over loops. It is interesting to note here that UPD peaks are discernible in all sweep rates which become more prominent at higher sweep rates. The simultaneous occurrence of UPD peak and characteristic cross over loops in the over-potential region (curves A & B, Fig. 5) is in contrast to the reported postulate [11] that the occurrence of UPD metal should result in 2 D layer-by-layer growth and the absence of UPD to 3D nucleation and subsequent crystal growth. It may be remarked here that similar

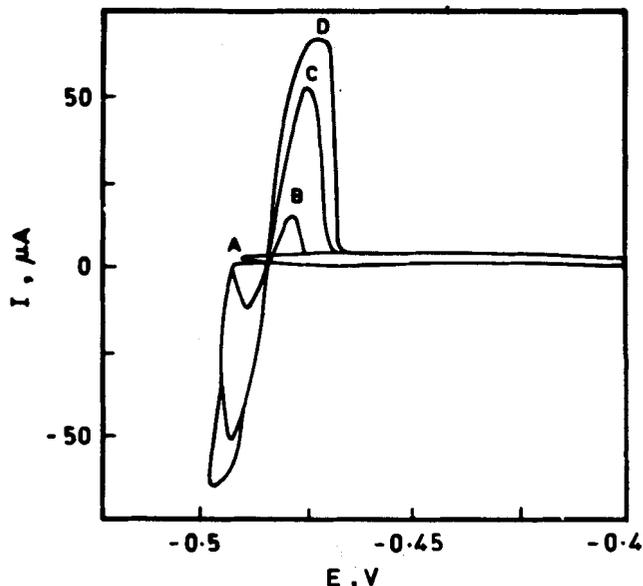


Fig. 4: Effect of varying the lower limiting potential [E(T)] of triangular scans during the OPD of 0.1 M Pb(NO₃)₂ in 1 M KNO₃ on GCE. E(T) = -0.491, -0.492, -0.495 and 0.498 V vs NCE for curves A, B, C and D respectively.

observations were made during the ECPF studies of copper on GCE [3] where the UPD peak occurs with an underpotential shift as expected [5].

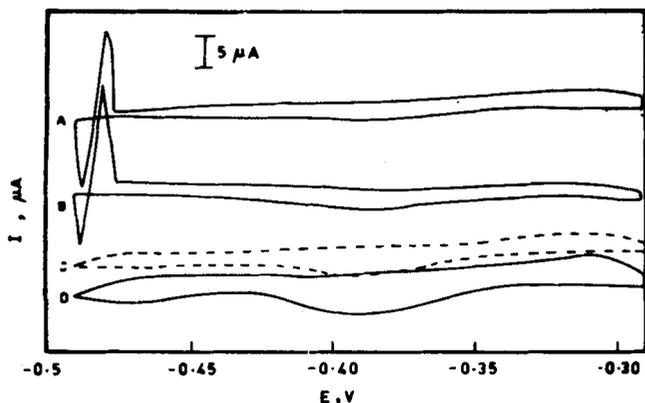


Fig. 5: Effect of sweep rate (V) on the deposition of 0.1 M Pb(NO₃)₂ in 1 M KNO₃ on GCE V = 6, 11, 30 and 50 mV/s for cyclic voltammograms A, B, C and D respectively.

Fig. 6 shows the effect of sweep rate on the deposition of 0.01 M lead in 1 M KNO₃ solution on to GCE by restricting the cathodic limit of the triangular scan to -0.55 V. The occurrence of cross-over loops with similar characteristics as in the case of 0.1 M lead (cf. Fig. 5) indicates that OPD occurs by 3D nucleation and subsequent crystal growth processes in this case also. Further, the constancy of cross-over potential with change in sweep rate clearly proves that the OPD processes are under interfacial control throughout the range of sweep rates studied.

The characteristic surface growth loops are absent when the OPD studies are carried out from 0.001 M lead in 1 M KNO₃ either by effecting changes in sweep rate or cathodic limit of the triangular scan indicating a 2D layer-by-layer growth processes. Thus, the nature of OPD of lead on GCE i.e. 3D nucleation and subsequent crystal growth or 2D layer-by-layer growth, seems to depend mainly on the concentration of

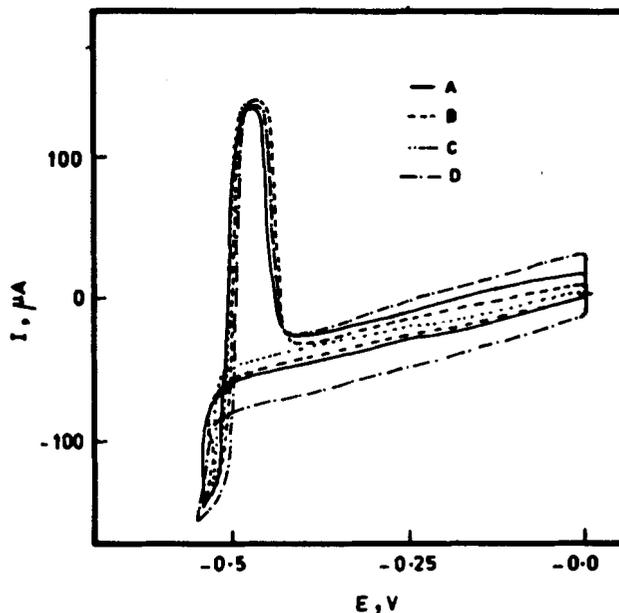


Fig. 6: Effect of sweep rate on the deposition of 0.01 M Pb(NO₃)₂ in 1 M KNO₃ on GCE V = 3, 6, 11 and 30 mV/s for cyclic voltammograms A, B, C and D respectively.

the depositing metal and is independent of the presence of UPD. Studies were then directed to elucidate the role of the substrate material on the OPD processes of lead by choosing graphite as alternate substrate.

OPD studies of lead on graphite

The multilayer formation of lead over graphite substrate was next investigated by subjecting to triangular scans of potential as described above [10] for GCE surface. The reversal of triangular scans in the initial stages of crystal growth results in the occurrence of cathodic current maximum immediately after scan reversal when the lead concentration is maintained at 5 × 10⁻², 10⁻² and 10⁻³ M (cf. Fig. 7). The occurrence of these surface growth loops indicate that OPD of lead occurs by 3D

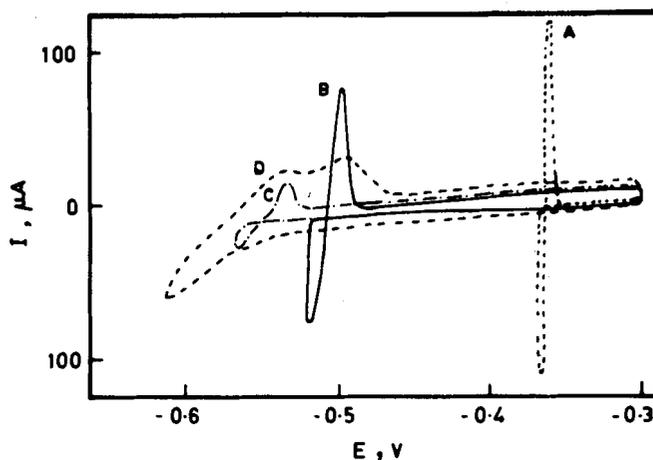


Fig. 7: I-E curves obtained using triangular scans of potential at 11 mV/s for the OPD of lead in 1 M KNO₃ solution on graphite. Curves A, B, C and D are for 5 × 10⁻², 10⁻², 10⁻³, and 10⁻⁴ M concentrations of lead respectively.

nucleation and subsequent crystal growth processes on graphite also. However, such cross-over loop is not seen when the concentration of lead is decreased to 10^{-4} M indicating that OPD in this case occurs by 2D layer-by-layer growth processes [11, 12]. It is interesting to note here that the occurrence of characteristic cross-over loops are seen at concentrations $\geq 10^{-2}$ M in case of GCE and $\geq 10^{-3}$ in case of graphite. This difference is attributed to the nature of substrate.

The effect of sweep rate on the OPD of 0.01 M lead onto graphite was next investigated. As seen from Fig. 8, the variation of sweep rate in the range 3 to 50 mV/s after restricting the cathodic limit of the triangular scan to -0.53 V, shows identical features as described above in the case of GCE i.e. the occurrence of cross-over loop and constancy of the cross-

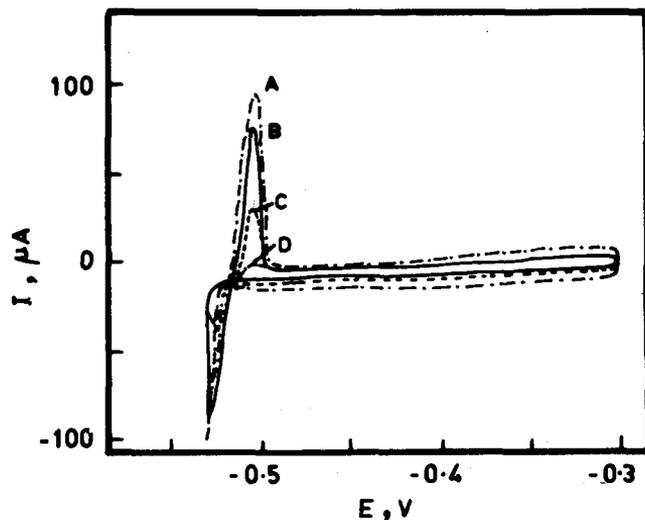


Fig. 8: Effect of sweep rate on the deposition of 0.01 M $\text{Pb}(\text{NO}_3)_2$ in 1M KNO_3 on graphite. $V = 3, 6, 30$ and 50 mV/s for cyclic voltammetric curves A, B, C and D respectively.

over potential. The latter characteristic suggests that OPD of lead follows interfacial-controlled kinetics during 3D nucleation and subsequent crystal growth processes over the range of sweep rates studied. Thus, it is concluded that the ECPF of lead in OPD region follows 3D nucleation and subsequent crystal growth or 2D layer-by-layer growth mainly dependent on the concentration of lead in solution and to a certain extent on the nature of the substrate. On the other hand, the occurrence of UPD seems to play little or no role on the mode of OPD of lead on GCE or graphite.

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