

ELECTROCHEMICAL PHASE FORMATION OF CALOMEL UNDER LINEAR POTENTIAL SWEEP CONDITIONS

G PRABHAKARA RAO, NAVIN CHANDRA AND G SUBRAMANIAN

Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

Electrocrystallization involved in electrochemical phase formation of anodic films is shown to manifest itself with characteristic features in current-potential response in potential sweep experiments that can be employed as diagnostic criteria. Results on calomel (Hg_2Cl_2) formation and growth on mercury are presented and discussed in the paper.

INTRODUCTION

Studies on electrochemical phase formation (ECPF) involving the nucleation and growth of deposits have been pursued with great interest in view of their importance in practical systems with the objective of understanding the kinetic steps involved in the initial stages of the new phase formation. Basic investigations on anodic films of different types using potentiostatic experimentation involving constant potential pulses have helped in arriving at a general formalism to explain the nucleation/growth phenomenon in such systems [1]. Very little is reported, however, on the application of potentiodynamic techniques (especially linear sweep voltammetry) for these studies although such techniques hold great promise in distinguishing clearly the possible alternate paths viz. adsorption, nucleation and growth, charge transfer and diffusion that may be encountered in the film growth in the initial stages. Detailed theoretical analysis of the electrochemical phase formation under potential sweep conditions and their application to electro-crystallization of metals have been the subject matter of a few recent reports [2-6]. This prompted the present authors to undertake the experimental investigations on anodic films under linear sweep conditions with a view to compare the results obtained on ECPF with those reported earlier using constant potential techniques. In this communication, the results of the experiments on the formation and dissolution characteristics of calomel (Hg_2Cl_2) from KCl solutions under cyclic potential sweep conditions using a wide sweep and concentration ranges are reported briefly.

EXPERIMENTAL

Cyclic voltammograms were recorded with Wenking Potentiostatic Model POS73 coupled with a digigraphic Model 2000, X-Y Recorder. Metrohm EA 290/2 hanging mercury drop electrode (HMDE) was used as working electrode. Platinum foil counter electrode and

Metrohm EA 491/5 Ag/AgCl (1M KCl) reference electrode (against which all potentials mentioned in this study are reported) were used with an all-glass cell. GR grade (Reechem) chemicals and double distilled water were used to prepare the required reagents. The solutions were deaerated by bubbling with pure nitrogen gas and all the measurements were carried out at $30^\circ \pm 1^\circ\text{C}$. A constant surface area of 0.1 sq.cm. in the HMDE was used throughout the studies. The same Hg drop was used for a series of measurements and the cyclic voltammograms were reproducible without any significant variation. The i-E curves were programmed in such a way that the anodic peak is not fully allowed to form but the scan direction is reversed at such anodic potentials by which a current loop is formed in the reverse scan. Depending on the reversal potential, the magnitude of the current in the cathodic direction will be more than the anodic one or vice versa. Such i-E curves were recorded for various scan rates ranging from 5 mV/sec to 100 mV/sec and for different concentrations of KCl from 0.05M to 1M. Cyclic voltammograms have also been recorded where the potential reversal is effected after the formation of calomel is complete, as manifested by anodic current peak, beyond which the current approaches zero and traces the cathodic path subsequently.

RESULTS AND DISCUSSION

Figures 1 to 6 depict the typical responses for the formation and dissolution of calomel under potential sweep conditions using different concentrations of KCl or sweep rates, and potential reversal at various stages of formation of calomel.

Figure 1 typifies the response noted under all the concentrations

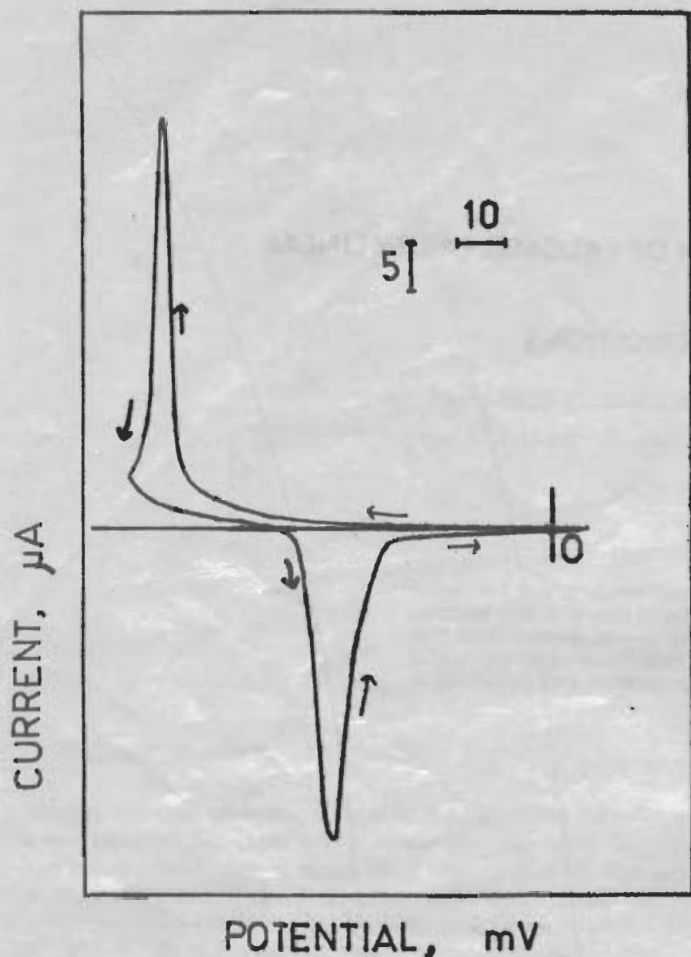


Fig. 1 : Typical potential sweep voltammogram for deposition and dissolution of calomel in 0.5M KCl. Anodic sweep to 0.09V, sweep rate = 10 mV/sec.

and sweep rates studied and represents the behaviour when the potential sweep covers the full range in the anodic direction over which the calomel is formed. The sharp rise in the anodic current giving a peak and the corresponding peak for reduction of calomel are characteristic features.

Figure 2 depicts the typical response obtained when the anodic

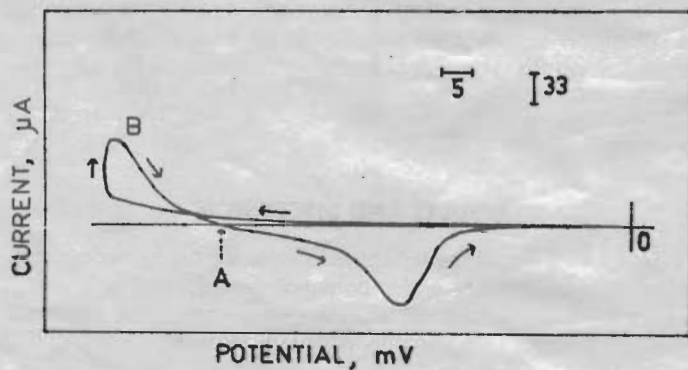


Fig. 2 : Typical potential sweep voltammogram showing the current loop formation (A) and inflexion point (B) concentration of KCl 0.5 M; Sweep rate = 50 mV/sec. Sweep reversal potential = 0.086 V.

potential sweep is reversed before the anodic peak occurs. The striking features of this type of response are (i) a sharp increase in anodic current, (ii) the occurrence of a current loop with a

maximum for the current between the anodic and cathodic course of the potential in the anodic potential region, (iii) a well-defined 'reversible' potential characterised by an inflection point at the intersection, and (iv) a cathodic stripping curve (for calomel) exhibiting a maximum. The changes brought about by extending the anodic limit of the sweep under otherwise identical conditions can be seen by a typical comparison of figures 2 and 3. The large

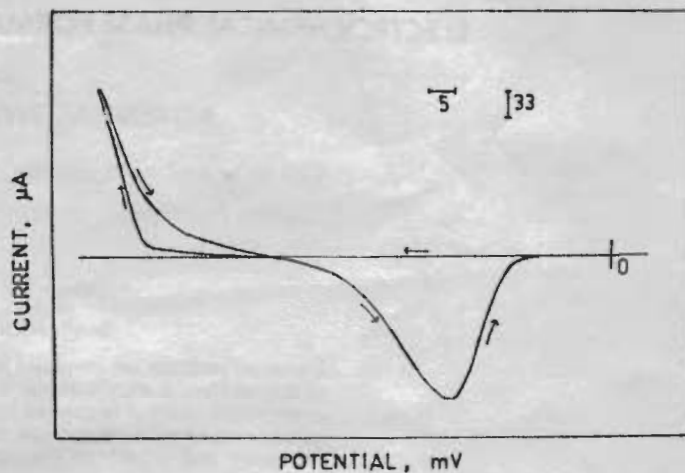


Fig. 3 : Same as Fig. 2 except the sweep reversal potential corresponds to 0.096 V.

and enhanced current for cathodic peak and charge associated with it are apparent though the anodic profile is qualitatively similar in both cases.

The response in concentrated solutions of KCl given in figure 4

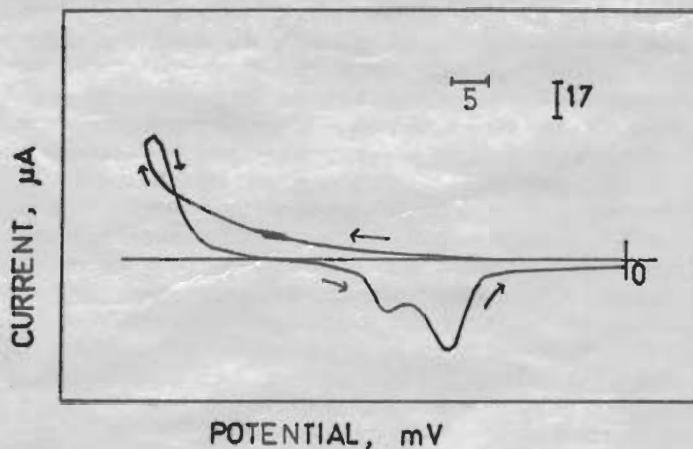


Fig. 4 : Potential sweep voltammogram for the deposition and dissolution of calomel in 1M KCl. Sweep rate 5 mV/sec. Potential of reversal 0.068 V.

also gives the expected current loop, current maxima immediately after the reversal of potential and the characteristic cross-over potential. However, the cathodic peak splits into two.

Figure 5 demonstrates similarly an additional feature in the form of a 'prepeak' in the anodic region typically noticed in dilute

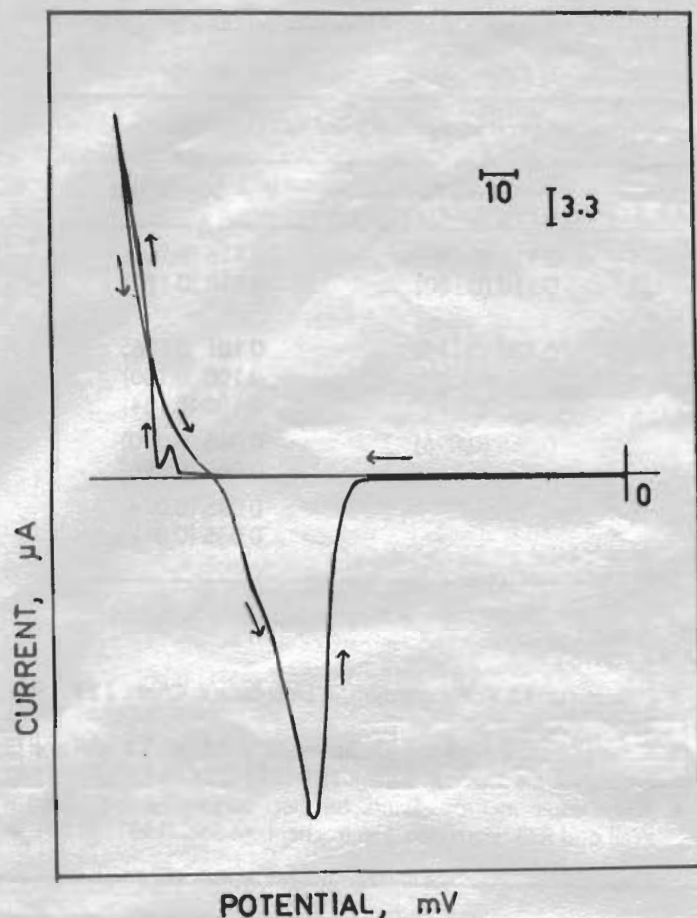


Fig. 5 : Same as figure 4; concentration of KCl = 0.05 M. Sweep rate = 10 mV/sec, Potential of reversal = 0.14 V.

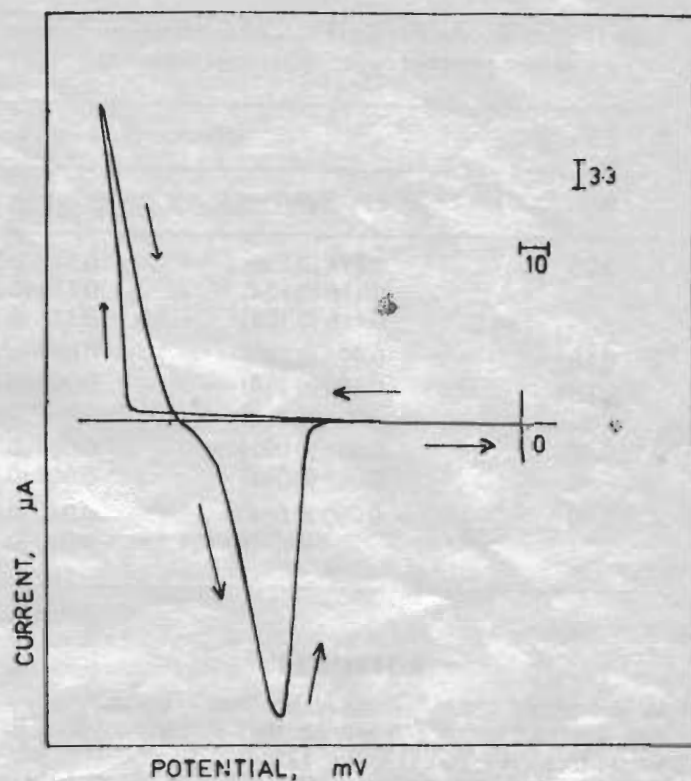


Fig. 6 : Same as figure 5 except the sweep rate 20 mV/sec.

solutions and especially at slow sweep rates. The absence of 'prepeak' by changing the sweep rate is illustrated in the corresponding figure 6. Figures 5 and 6 also highlight another important difference in loop characteristics that is noticed throughout these investigations, viz. the magnitude of current after reversal can be large or small compared with the same before reversal (at a given potential).

The various observations noted above conform to the expectations based on a mechanism involving electrocrystallization for calomel under all conditions of experimentation. Thus the sharp rise in the anodic current may be taken to characterise the onset of crystal growth of calomel, and the current loop observed between the anodic and cathodic course of the potential in the anodic region substantiates the same. These findings on anodic film formation through electrocrystallization are analogous to similar observations on cathodic deposition of metals involving their electrocrystallization [5]. In the case of metal deposition, it has been theoretically predicted and experimentally verified that if forward (cathodic) scans of triangular potential are reversed before intercrystal collisions occur, then maximum in current can be seen on reverse scans when the growth rates of crystals are not explosive functions of potential and can be used to diagnose nucleation/growth kinetics since neither adsorption nor charge transfer/diffusion kinetics ever exhibit such behaviour generally [5]. The results obtained on calomel growth reported here provide evidence to the fact that the above considerations are equally applicable to the anodic crystallization phenomenon. The data on constant cross-over or inflection point (where the current changes its polarity from positive to negative) for a given

concentration (refer Table I) independent of sweep rate and reversal potential noticed provides additional confirmation for the above and further suggests that the crystal growth is under interfacial control [5].

One interesting feature in electrocrystallization of calomel, however, is worthy to note. This refers to the aspect relating to the magnitude of current after potential reversal being higher or lower than the corresponding current at a given potential, in the loop region depending on the experimental conditions employed while one notices always only higher currents in the case of metal deposition. This may be understood as follows. In the case of calomel, it is known that the anodic film formation is associated with passivation and hence depending on the extent of calomel film formation, one can encounter higher or lower currents after the reversal. This is typically brought out in figures 5 and 6 (where the effect of passivation is reflected in lower currents at low sweep rate in figure 5 while no such thing is noticed in figure 6 recorded using a higher sweep rate). Further it is interesting to see from the above figures that the cross-over point is unaffected.

The establishment of the mechanism through electrocrystallization under potential sweep conditions and also the extraction of the kinetic parameters for the same are also possible through the analysis of peak current and peak potential characteristics and their dependence on scan rate through the use of the theoretical formalism reported recently [4] for monolayer growth but could not be carried out as the deposits reported here are all more than several monolayers.

Further work is in progress to provide results in this direction as well as to fully understand the origin of the additional features that are briefly reported here viz. the splitting of the cathodic stripping peak of calomel and the anodic 'prepeak'.

Table I: Data on inflection point noticed under different sweep rates and concentrations (Values in brackets denote the limit of the anodic potential sweep or reversal potential)

No.	Conc. of KCl (M)	Inflection point for various sweep rates 'V' (Volt vs Ag/AgCl-1M KCl)			
		V = 5 mV/sec	V = 10 mV/sec	V = 20 mV/sec	V = 50 mV/sec
1.	0.05	0.114 (0.130)	0.115 (0.130)	0.115 (0.140)	0.116 (0.160)
		0.116 (0.134)	0.114 (0.134)	0.118 (0.150)	0.118 (0.170)
		0.116 (0.138)	0.115 (0.138)	—	—
2.	0.10	0.99 (0.120)	0.099 (0.110)	0.100 (0.116)	0.101 (0.136)
		0.100 (0.118)	0.099 (0.114)	—	0.100 (0.150)
		—	0.100 (0.118)	—	0.100 (0.154)
3.	0.50	0.067 (0.092)	0.065 (0.096)	0.065 (0.096)	0.065 (0.090)
		0.067 (0.094)	0.068 (0.094)	—	0.065 (0.096)
4.	1.00	0.050 (0.068)	0.046 (0.070)	—	0.045 (0.074)
		—	0.047 (0.070)	—	0.045 (0.81)

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