Cyclic voltammetric studies on gallium film electrodes in alkaline media

A VARADHARAJ and G PRABHAKARA RAO*

Central Electrochemical Research Institute, Karaikudi 623 006, India

Abstract. Using cyclic voltammetric techniques the electrochemical behaviour of gallium in alkali media has been investigated. Three anodic peaks, one cathodic peak, and a secondary anodic peak – an observation hitherto unreported – are obtained. Detailed analyses of these various stages of oxidation and reduction based on their peak potential and peak current characteristics have revealed the nature of the underlying electrochemical reactions.

Keywords. Cyclic voltammetry on gallium; anodic oxidation of gallium; mechanism of oxide film growth.

1. Introduction

Studies of the electrochemistry of gallium particularly in alkaline media are important from the view point of its recovery from Bayer's liquor – one of the chief sources for gallium. Yet the electrochemical behaviour of gallium in alkaline solutions is not fully understood as revealed by the survey of literature on the subject (Bockris and Enyo 1962; Armstrong *et al* 1971; Perkins 1972, 1979; Bard 1978). This is largely because of the difficulty in handling this readily oxidised metal and the large influence of impurities and surface oxides on its properties.

A perusal of the studies reported so far on the electrochemical behaviour of liquid and solid gallium electrodes in alkali media reveals that there is no unanimity among different workers particularly about the oxidation behaviour of gallium. It is realised by all that much of the uncertainty in the polarisation data in alkaline media is associated with the "ever present" oxide or hydroxide passive films that are part of most gallium working electrodes. As such, mechanisms were proposed more on the basis of speculation and less on that of experimental findings which are difficult to reproduce for reasons mentioned above.

In a previous communication, we briefly reported a gallium film electrode (prepared *in situ*) that yields reliable and reproducible polarization data, indicating its potential in kinetic studies (Varadharaj and Prabhakara Rao 1982; Varadharaj 1984). In this work we present the results of our studies on the electrochemistry of gallium in alkaline media using such an electrode and the cyclic voltammetric (CV) technique: These results, obtained and reported for the first time, enable us to elucidate clearly the mechanism of the different stages of the anodic oxidation of gallium and its reduction under cyclic voltammetric conditions.

---

* For correspondence

2. Experimental

A conventional all-glass electrolysis cell, with provision for an inlet and an outlet for deaerating the solution with pure N_2 gas, was used. A three-electrode system consisting of copper rod sealed in teflon (area $0.283\,cm^2$) on which the gallium film was formed (working electrode), platinized platinum counter electrode, and Hg/HgO in 1M NaOH reference electrode were employed. The details of electrode preparation and its evaluation have been discussed elsewhere (Varadharaj and Prabhakara Rao 1982).

The potential of the working electrode is controlled by a Wenking potentiostat Model LB 75M coupled with a VSG-72 scanning generator. An x-y recorder (Digitronic Model 2000 series) is used to record the I-E curves. The range of potential covered is -1.6 to -1.0V Vs Hg/HgO in 1M NaOH. The measurements are made at $25 \pm 1°C$.

3. Results and discussion

The cyclic voltammogram (CV) consists of the H_2-evolution region (-1.55V and above) followed by three anodic oxidation regions (shown as A1, A2 and A3) on the forward sweep under all sweep rates and concentration conditions studied (see figure 1). One cathodic peak (shown as C1) on the reverse sweep has been noted at sweep rates above $80\,mVs^{-1}$ in all solutions of alkali strength corresponding to 0.1–1.0M NaOH. In alkali concentrations above 1.0M the C1 peak could be noticed only at sweep rates higher than $200\,mVs^{-1}$. An additional "secondary anodic peak" (shown as A* figure 1b) has been observed during the reverse (negative) sweep under certain sweep rates (less than $40\,mVs^{-1}$) only when the concentration of alkali is 1.0M or less and in the higher alkali concentration, viz. above 1.0M, under all sweep rates employed.

The peak potential values of three anodic oxidation regions viz. E_p (A1), E_p (A2) and E_p (A3) have been found to vary with alkali concentrations at a fixed sweep rate. The peak A1 shifts negatively with increasing concentrations, the shift amounting to $\simeq 40\,mV$ (table 1). Values of E_p (A1) are found to be almost independent of sweep rate for a given concentration of alkali. The peak potential values of E_p (A2) are found to shift to more positive values with increasing sweep rate for a given alkali strength (see figure 2). The peak potential values of E_p (A*) almost coincide with E_p (A1) and are independent of sweep rate for a given alkali concentration.

The peak current values of A1, viz. i_p (A1), are independent of alkali strength at a fixed sweep rate, while the peak currents of A2 and A3 [viz. i_p(A2) and i_p(A3)] increase with alkali strength. Values of i_p (A1), i_p (A2) and i_p (A3) are found to increase with increasing sweep rate for a given concentration. It is noted that the magnitudes of i_p (C1) are not so significant under most of the experimental conditions reported here.

The anodic peak, A1, observed in this work on gallium film electrodes in the potential range -1.375 to -1.420V, is an accordance with the observations reported earlier by Armstrong *et al* (1971) and Perkins (1972, 1979). The experimentally observed independence of E_p (A1) and also E_p (C1) with regard to scan rate, together with the observation of $[E_p(A1)-E_p(C1)]$ amounting only to about $5\,mV$, suggests a surface reaction of a reversible type in this region rather than a reaction involving soluble species. The i_p(A1) values, when plotted against the sweep rate, v, yield linear plots as given in figure 3. The observed linear dependence of peak height, $i_p(A1)$ on scan rate is also consistent with the expectation based on a surface reaction (Srinivasan
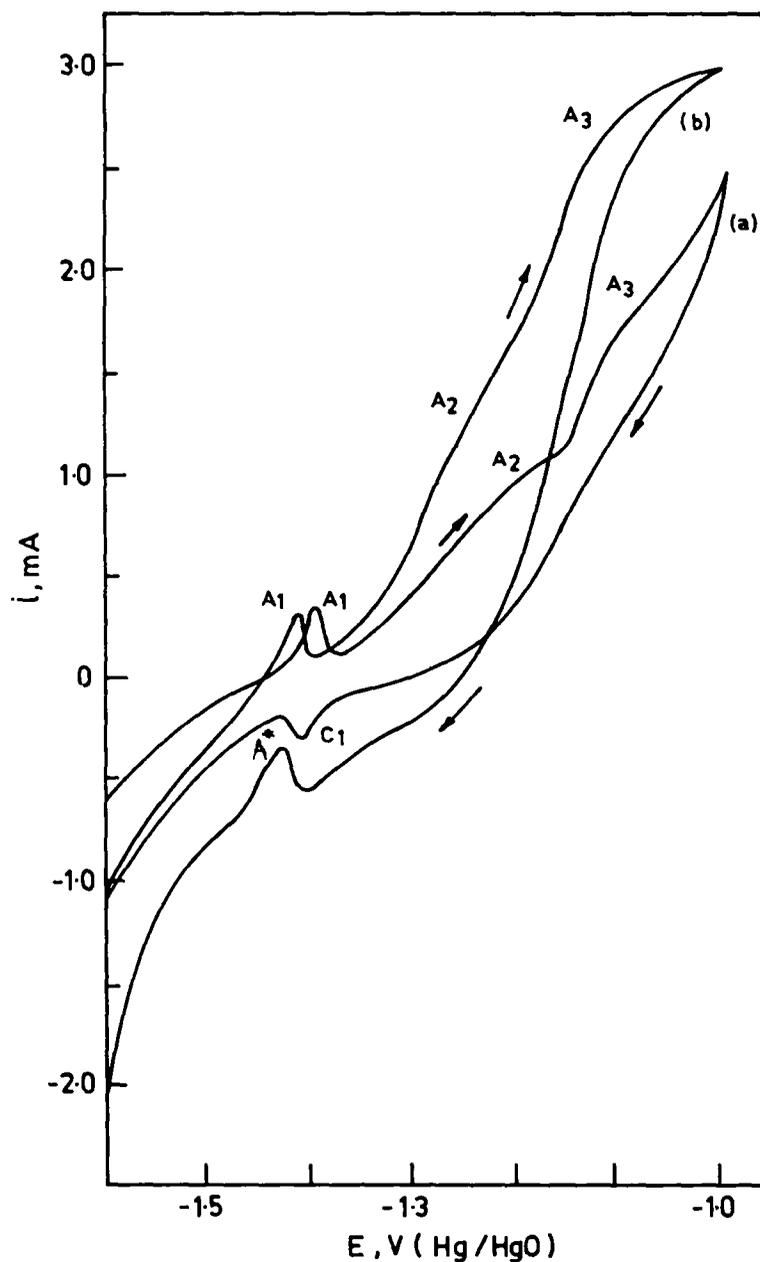
Figure 1. Cyclic voltammogram of gallium film electrode in (a) 0·5M NaOH, sweep rate 100 mVs^{-1}, and (b) 3·0M NaOH, sweep rate 40 mVs^{-1}.

and Gileadi 1966). Thus, the characterization of the peaks A1 and C1 as arising due to surface film formation and its reduction, respectively, giving the supporting experimental data, is presented in this study. Unlike as in earlier reports, the A1 could be obtained as a well-defined peak in the present work. The characteristics noted for the C1 peak under different alkali concentrations suggest that the film formed under

Table 1. Data on potential values of anodic peak, A1, obtained under different alkali concentrations and sweep rate, v.

v	(NaOH)/M				
(mVs^{-1})	0·1	0·5	1·0	2·0	6·0
5	−1·380	−1·400	−1·405	−1·410	−1·420
10	−1·380	−1·400	−1·405	−1·410	−1·420
20	−1·385	−1·390	−1·405	−1·405	−1·420
40	−1·385	−1·390	−1·400	−1·405	−1·420
60	−1·385	−1·390	−1·405	−1·405	−1·420
80	−1·380	−1·390	−1·400	−1·405	−1·420
100	−1·380	−1·390	−1·400	−1·405	−1·420

A1 is more soluble in very alkaline solutions. Considering the charge associated with peak A1 (table 2) a monolayer thickness in 0·1 M NaOH could be inferred under low sweep rate conditions. Our results on computing charge under A1, with different concentrations and sweep rates, indicate oxide growth upto four layers at low sweep rates and at alkali concentrations less than 1·0M. Perkins (1972, 1979) however invoked the growth of multilayers in the A1 region by computing charge under C1. Increase in alkali concentration beyond 1·0M NaOH resulted in decreasing charge which is noticed uniformly at all the sweep rates studied. Hence, a concentration of 1·0M NaOH is seen to be the optimum for maximum film formation.

For obtaining the number of electrons transferred in the oxidation step under A1 two approaches have been followed that yield identical results. In the first one, the experimentally observed Ep shifts of A1 with hydroxyl ion concentration have been employed for constructing Ep vs log a_{OH} plots which according to Abd El Haleem and Badr G Ateya prove useful in arriving at the n values for the oxidation of copper in alkali (Delahay 1954; Abd El Haleem and Ateya 1981). The plots yielded a straight line whose slope is equated to $(59/n)$mV. The value of n thus calculated was three. In another approach based on the Tafel plots, obtained from the analysis of the data at the ascending portion of the foot of the A1 wave, the number of electrons involved was computed (Reinmuth 1960). Linear plots are obtained when potential is plotted vs the logarithm of current. The typical Tafel plot, obtained for the A1 peak in 6·0M NaOH using sweep rates 10 and 20mVs^{-1}, are given in figure 4A. The slope of the Tafel plots obtained is 40 ± 5mV under almost the entire range of concentrations of alkali employed at various sweep rates. Assuming a value of 0·5 for transfer coefficient, the n values computed were consistent with the expectations based on three-electron transfer (table 3). Parallel shifts of tafel plots are observed at all concentrations and sweep rates employed. It may be remarked here that the presence of irreversible oxidation steps (beyond the A1 region) on the anodic cycle, coupled with the likely area change of the electrodes under those conditions, might be responsible for this parallel shift noted in the CV curves at the foot of the wave in the repeated cycles.
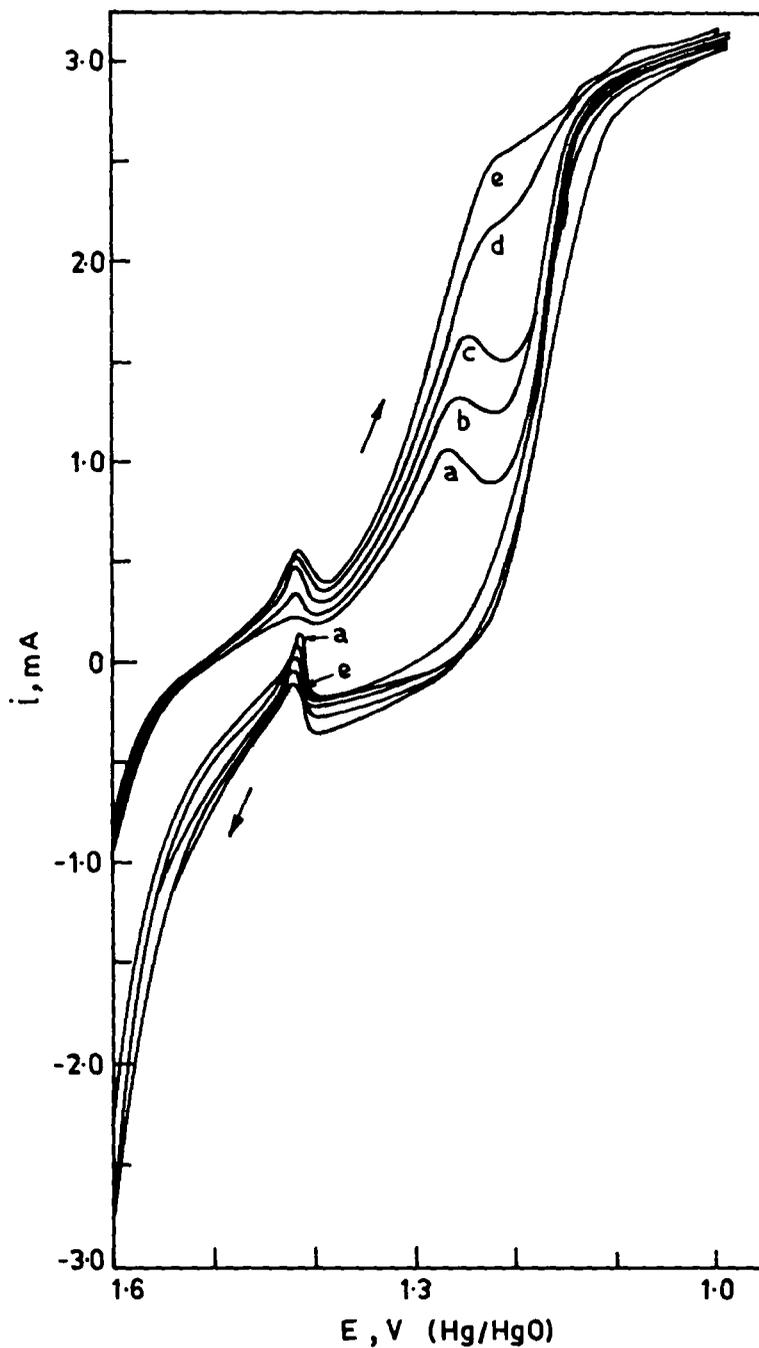
Figure 2. Effect of voltage scanning rate on the cyclic voltammograms of gallium film electrode in 6·0M NaOH (a) 5, (b) 10, (c) 20, (d) 60, and (e) 100 mVs⁻¹.
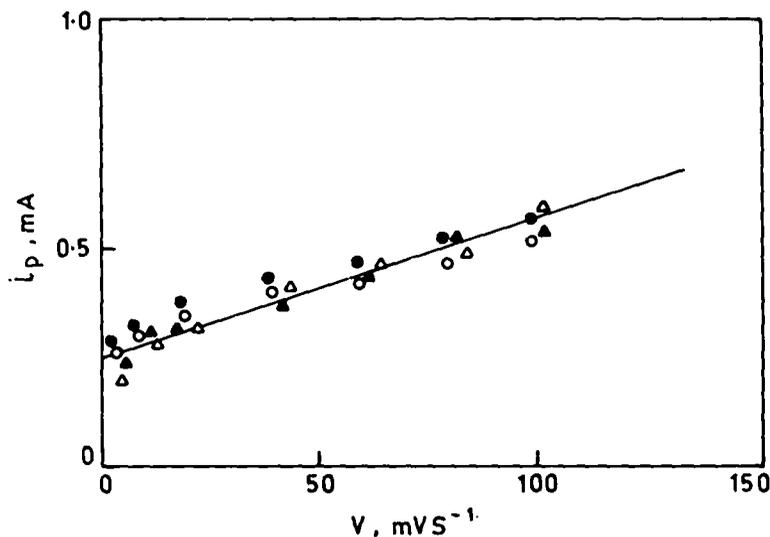
Figure 3. Plots of peak current, i_p vs sweep rate of anodic peak A1 for different concentrations of alkali solution: ($\bigcirc$) 0·5, ($\bullet$) 2·0, ($\blacktriangle$) 4·0, and ($\triangle$) 6·0M NaOH.

Table 2. Quantity of anodic charge, $\mu c/cm^2$, obtained for anodic peak, A1, under different alkali concentration and sweep rate, v.

v (mVs^{-1})	(NaOH)/M				
	0·1	0·5	1·0	2·0	4·0
5	706·7	2081·5	2997·0	1831·5	—
10	624·4	1290·4	1748·2	1623·4	—
20	353·8	770·1	1061·4	1040·6	728·4
40	260·0	347·5	645·0	686·8	478·4
60	208·1	312·2	485·6	513·4	367·7
80	187·3	260·1	421·4	468·3	301·8
100	187·3	216·4	358·0	395·4	258·1

In the alkaline media the pH potential diagram of Pourbaix suggests the following equilibria.

$$Ga + 3H_2O \rightleftharpoons Ga(OH)_3 + 3H^+ + 3e, \qquad (A)$$

$$2Ga + 3H_2O \rightleftharpoons Ga_2O_3 + 6H^+ + 6e, \qquad (B)$$
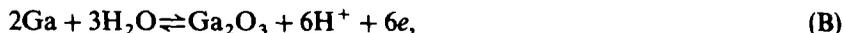
that are relevant for the present purpose.

Although the number of electrons transferred in both the oxidation reactions (A) and (B) corresponds to three, the nature of the oxidation product is slightly different. Consideration of the peak potential data observed under varied experimental conditions along with the reactions represented in (A) and (B) suggests the possibility of the oxidation of gallium through step (A) with the alkali concentration < 1·0M NaOH. The less positive peak potentials noted in alkali concentration > 1·0M NaOH seem to involve the step (B). Unlike in earlier reports, the present experimental results offered an understanding of the domains of steps (A) and (B) with supporting evidence.
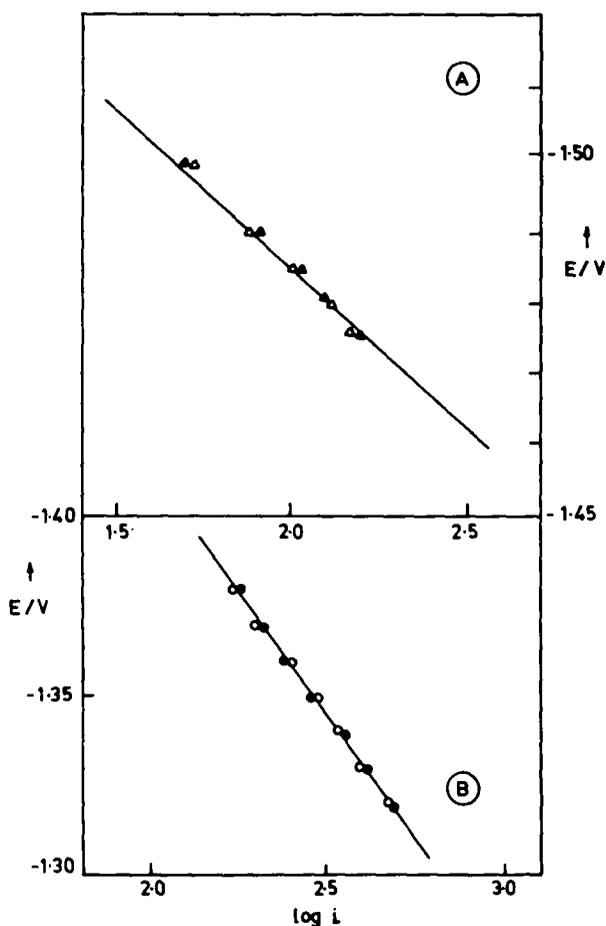
Figure 4. Tafel plots obtained from the foot of the anodic peaks (A) A1 in 6·0M NaOH using sweep rates of (△) 10 and (▲) 20 mVs⁻¹, (B) A2 in 5·0M NaOH using sweep rates of (○) 5, and (●) 10 mVs⁻¹.

Table 3. Values of number of electron, n calculated from the Tafel slope value obtained from the analysis of the foot of the A1 and A2 peaks for different alkali and sweep rate conditions.

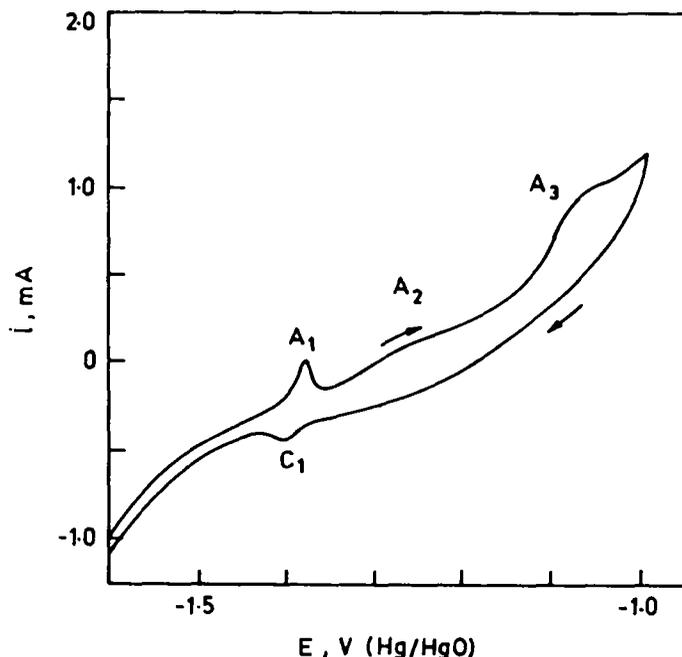| v (mVs⁻¹)	Alkali concentration (M)							
	(A1 peak)				(A2 peak)			
	0·5	1·0	2·0	6·0	0·5	1·0	2·0	6·0
10	—	2·6	3·2	2·7	1·0	0·9	1·3	0·9
20	—	2·6	3·3	2·7	0·90	0·8	1·2	0·8
40	2·8	2·6	3·3	2·7	0·90	0·8	1·0	0·8
60	2·6	2·6	3·3	2·7	0·92	0·8	1·0	0·9
80	2·6	2·6	3·3	2·7	0·92	0·8	0·9	0·9
100	2·7	2·6	3·3	2·7	0·92	0·8	0·9	0·9

Figure 5. Cyclic voltammogram of gallium film electrode in 0·1M NaOH, sweep rate 80 mVs^{-1}.
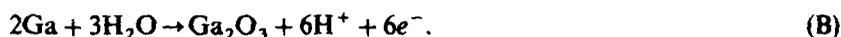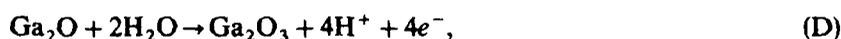
The appearance of peak A1 below the zero current line in a narrow alkali concentration of 0·1 and 0·2M NaOH (figure 5) noticed in the work (on solid Ga film) is in contrast to normal expectation and also to the observations reported by Armstrong *et al* (1971) and Perkins (1972, 1979) under identical alkali concentration (on liquid Ga). In the above quoted works resolution of the various oxidation states was poor at slower sweep rates in contrast to the clear-cut separations noticed in the present work. This is believed to be due to the difference in the nature of the working electrodes employed in the respective cases. It is well-known that passivation of the gallium surface imparts irreproducible polarization data and liquid gallium is much inferior in this respect as compared to a solid electrode (Lezhava and Vagramyan 1965). Corrosion of gallium occurs even in dilute alkali solution which is expected to dominate under alkali concentrations of 0·1 and 0·2M. Hence, the observed negative currents associated with A1 are presumed to be the result of concomitant hydrogen evolution (Hurlen and Valand 1964).

The formation of A2 peak using the gallium film electrode is well-defined and occurs over the potential range − 1·190 to − 1·295 V. The irreversible nature of this peak was apparent from the observed shift of the peak potential with sweep rate for a given concentration of alkali and the absence of the corresponding reduction peak on reversing the potential sweep. An analysis of the peak A2, attempted and described below, is a noteworthy feature of the present work, with no similar attempts having been reported earlier.

Data on the ascending portion of the foot of the A2 wave for Tafel behaviour, revealed that linear plots are obtained when potential is plotted against logarithm of current. The typical Tafel plot, obtained for the A2 peak in 5·0M NaOH using sweep

rates of 5 and $10 \, \text{mVs}^{-1}$ are given in figure 4B. The slope of the Tafel plots obtained is seen to be $120 \pm 20 \, \text{mV}$ under the entire region of concentration studied. Assuming a value of 0·5 for the transfer coefficient, the slope is in conformity with a one-electron transfer process (table 3). The number of electrons computed, based on $E_p - E_p/2 = (48/\beta na) \, \text{mV}$ relationship, are seen to approximate to either two or three depending on the experimental conditions (assuming $\beta = 0·5$). Thus for example data on alkali strength upto 1·0M and fast sweep rate conditions (upto $40/60 \, \text{mVs}^{-1}$) suggest a two-electron transfer while under slow sweep rate conditions a three-electron transfer is indicated. But above 2·0M NaOH a uniform two-electron transfer is suggested under all sweep rates employed.

A tentative mechanism based on the scheme given below, which takes into account the relevant electrochemical reactions in alkaline media, satisfies the above experimental observations.

$$2Ga \overset{H_2O}{\rightleftharpoons} Ga_2O + 2H^+ + 2e, \tag{C}$$

$$Ga_2O + 2H_2O \rightarrow Ga_2O_3 + 4H^+ + 4e^-, \tag{D}$$

$$3Ga_2O \xrightarrow{\text{disproportionate}} 4Ga + Ga_2O_3, \tag{E}$$

$$2Ga + 3H_2O \rightarrow Ga_2O_3 + 6H^+ + 6e^-. \tag{B}$$

The formation of Ga_2O, (C), involving a single electron transfer, may account for the observations noted at the foot of the A2 region. Ga_2O being an unstable product can be expected to disproportionate giving Ga metal and Ga_2O_3 as per (E). Further oxidation may be decisively influenced by this disproportionate step (E). Results obtained on HMDE and glassy carbon electrode in alkaline gallate medium suggest a similar disproportionate mechanism (Varadharaj and Prabhakara Rao 1984, 1989).

At low alkali (upto 1·0M NaOH) and fast sweep rates the disproportionation kinetics may not occur significantly and the oxidation of Ga_2O can smoothly proceed through the step (D) to give Ga_2O_3 involving a two-electron transfer. On the other hand, under low alkali and slow sweep rates, one can envisage pronounced accumulation of Ga_2O and its disproportionation to Ga_2O_3 and Ga via (E). So the oxidation of Ga can now occur involving a three-electron transfer through (B). The two-electron transfer noticed in concentrations greater than 1·0M NaOH, independent of sweep rates employed, can also be explained by the above scheme satisfactorily as one expects the step (D) to predominate in highly alkaline solutions. Thus the change over of mechanism from a two- to a three-electron transfer under different alkali and sweep rates can be seen to follow from the above scheme in the alkali regimes employed.

The appearance of A3 is seen to be closely linked with the characteristics of the A2 peak. For example when A2 is well-formed, typically at slow sweep rates and high concentrations, the formation of A3 is seen to be feeble. On the other hand the feeble appearance of A2 under high sweep rates results in A3 formation. This general trend can be seen to be valid for all the concentrations of the alkali and sweep rates studied. It is also noted that A3 does not appear over an intermediate range of alkali concentrations (viz. 0·7 to 1·0M NaOH) in all sweep rates employed. Similarities of the anodic peaks under A2 and A3 under a variety of experimental conditions seem to be in support of the suggestion made by Perkins (1972, 1979) earlier that the A3

peak arises as a result of the oxidation of the unreacted species under A2. For example A3 invariably appears under fast sweep rates ($>60\,mVs^{-1}$) which may be the result of insufficient oxidation of Ga_2O to Ga_2O_3 under A2 in the limited time of the scan. The concentrations of 0·7 to 1·0M NaOH are perhaps suited for favourable quantitative conversion of Ga_2O under A2 itself and, hence, the total absence of A3 under such conditions.

The features exhibited in the cathodic part of the cyclic voltammograms are very much dependent on the experimental conditions employed. A cathodic reduction process C1 and an anodic process, A*, manifest themselves during the cathodic sweep. The appearance of A* is the new observation in this work that aided in furthering our knowledge of gallium electrochemistry in alkaline media. The potential regime over which the C1 and A* appeared strongly suggest the inter-relationship of the underlying reactions involving these two species.

As already discussed, the likely product under A1 is $Ga(OH)_3$ or Ga_2O_3 film that grows to a few monolayers. Now, the peak potential value of C1 corresponding to the reduction of the above film is in agreement with the expectations based as a reversible surface reaction.

The cathodic peak C1 is conspicuous by its absence whenever A* appears and the appearance of A* is confined to pure alkali solution and its concentration. In general, low sweep rates ($<40\,mVs^{-1}$) and high concentrations of alkali promote A* formation. The various experimental observations can be understood in terms of the formation of a lower-valent intermediate (during the forward sweep) such as monovalent gallium species under favourable conditions whose oxidation is seen under A* (in the reverse sweep). Formation of lower-valent species have been suggested earlier during electrochemical polarisation of gallium (Selekhova *et al* 1972).

Finally the appearance of only one or the other of these peaks, C1 or A* may be associated with the time constants of the formation and dissolution of trivalent gallium species on the one hand and the formation and oxidation of the monovalent gallium species on the other vis-a-vis the sweep rates employed in the experiment.

Acknowledgement

References

Abd El Haleem S M and Ateya B G 1981 *J. Electroanal. Chem.* 117 309
Armstrong R D, Race W P and Thirsk H R 1971 *J. Electroanal. Chem.* 31 405
Bard A J (ed.) 1978 *Encyclopaedia of electrochemistry of the elements* (New York: Marcel Dekker) vol. 8, p. 207
Bockris J O'M and Enyo M 1962 *J. Electrochem. Soc.* 109 48
Delahay P 1954 *New instrumental methods in electrochemistry* (New York: Interscience) chap. 6
Hurlen T and Valand T 1964 *Electrochim. Acta* 9 1433
Lezhava T I and Vagramyan 1965 *Sov. Electrochem.* 1 275
Perkins R S 1972 *J. Electrochem. Soc.* 119 713
Perkins R S 1979 *J. Electroanal. Chem.* 101 47
Reinmuth W H 1960 *Anal. Chem.* 32 1891

Selekhova N P, Lyubimova N A and Leikis D I 1972 *Elektrokhimiya* **8** 721

Srinivasan S and Gileadi E 1986 *Electrochim Acta* **11** 321

Varadharaj A 1984 *Some contributions to the electrochemistry of gallium – cyclic voltammetric studies in alkali and alkaline gallate solutions*, PhD thesis, Madurai Kamaraj University

Varadharaj A and Prabhakara Rao G 1982 *J. Electroanal. Chem.* **138** 189

Varadharaj A and Prabhakara Rao G 1984 *Proc. Third International Symposium on Advances in Electrochemical Science and Technology* (Karaikudi: SAEST)

Varadharaj A and Prabhakara Rao G 1989 *J. Electrochem. Soc., India* **38** 1