

Anodic current peaks during cathodic sweep in cyclic voltammetric studies on gallium film electrode in alkaline solutions

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A gallium film electrode (prepared 'in situ') yielded reliable and reproducible polarisation data, indicating its potentialities in kinetic studies. The cyclic voltammogram indicates the appearance of anodic peak during the cathodic sweep and has been noted in this work. The potential regime over which the anodic peak currents appeared, the effect of alkali concentration sweep rate and the reversal of voltage excursion at different potential regimes on the anodic peak current have been investigated. The resultant experimental observations indicate the formation of a lower valent intermediate to be responsible for yielding this anodic peak current.

Key words: Cyclic voltammetry, gallium film electrode, secondary anodic peak

INTRODUCTION

The electrochemical behaviour of liquid and solid gallium electrode in alkaline medium is not fully understood, because of the difficulty in handling this readily oxidized metal and the large influence of impurities [1]. A gallium film electrode (prepared "in situ") yielded reliable and reproducible polarisation data [2]. The cyclic voltammogram indicates the appearance of an additional anodic peak during the cathodic sweep (secondary anodic peak) in addition to the usual peaks normally observed and has been reported for the first time. In this communication a brief account of this secondary anodic peak and its dependence of sweep rate, alkali concentration, reversal of voltage excursion at different potential regimes etc. is reported.

EXPERIMENTAL

A three electrode system, consisting of gallium film working electrode, platinised platinum counter electrode and Hg/HgO in 1M NaOH reference electrode, was used. The range of potential covered was -1.6 to -1.0 V vs Hg/HgO. All the potentials were expressed vs Hg/HgO in 1M NaOH and the measurements were made at 298 ± 1 K. Sodium hydroxide solutions corresponding to 0.1-6M NaOH were employed.

RESULTS AND DISCUSSION

Figure 1 (curve a) gives a typical cyclic voltammogram recorded using 6M NaOH at the sweep rate of 40 mV.s^{-1} . The CV consists of three anodic peaks (shown as A1, A2 and A3) and an additional secondary anodic peak (shown as A*) observed during the negative sweep. The peak A* is

observed only under sweep rates $< 40 \text{ mV.s}^{-1}$ in low alkali concentration, and in high alkali concentration (i.e. $> 1\text{M}$ NaOH) under all sweep rates employed. $E_p(A^*)$ almost coincides with $E_p(A1)$ and is independent of sweep rate for a given concentration.

The results obtained in the experiments in which potential reversal has been effected at various stages of oxidation (viz. after A1, after A2 and after A3) reveal that the A* peak is enhanced when A2 is included (see Fig. 1b, 1c, and 1a). It is possible that the source for monovalent gallium is the product obtained at the foot of the wave A2 and this assumption justifies the observations on the A* made in programmed potential experiments. The inclusion of A3 showed no perceptible influence on A*. Another significant point to be noted is that the appearance of A* has always been associated with the disappearance of the cathodic peak and vice versa.

The above observations can be understood in terms of lower valent intermediate formation such as monovalent gallium species which have been involved earlier during electrochemical polarisation of gallium [3-5]. Finally, the appearance of cathodic peak or A* may be associated with the time constants of the formation and dissolution of trivalent gallium or monovalent gallium species vis-a-vis the sweep rates employed in the experiment.

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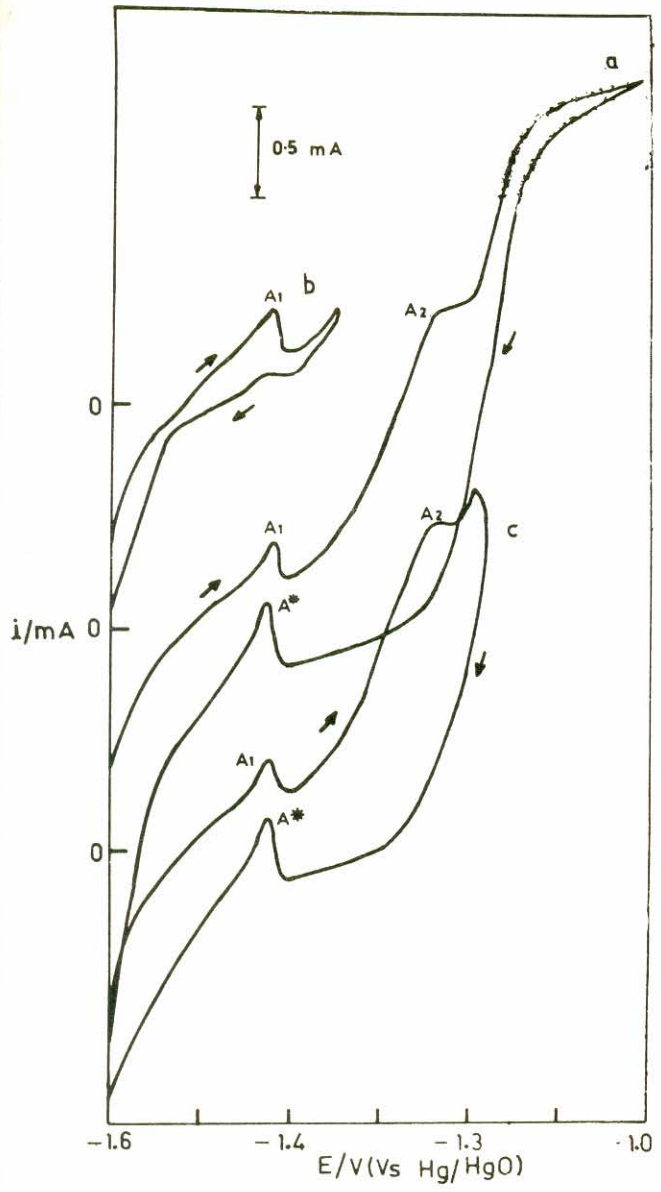


Fig. 1: Cyclic voltammograms of gallium film electrode in 6M NaOH at selected voltage excursion. Scan reversal effect at (a) -1.000 (b) -1.350 and (c) -1.200 V. Sweep rate 40 mVs⁻¹

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