ELECTROMETALLURGY AND THERMICS

EFFECTS OF CERTAIN IMPURITIES ON ALKALINE GALLATE REDUCTION —
A LINEAR STRIPPING VOLTAMMETRY STUDY

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Gallium is mainly electrowon from sodium aluminate solution (Bayer liquor) of aluminium industries by electrolytic method. The effective recovery of gallium is inhibited by the presence of metallic and organic impurities. Investigations on the effect of certain metallic impurities, employing linear sweep stripping voltammetry technique on rotating glassy carbon disc electrode revealed the inhibitive effect of these ions on gallium recovery process in alkaline medium.

Key words: Glassy carbon electrode, sodium gallate, linear stripping voltammetry

INTRODUCTION

Electrowinning of gallium from sodium aluminate solutions of aluminium industry is practised for many years now. Because of its close similarity in atomic radii with aluminium, gallium is invariably associated with bauxites to the extent of 0.002 to 0.005%. During the working cycle of aluminium, (Bayer process-digesting bauxite with alkali) gallium is taken into sodium aluminate solution as sodium gallate. Depending on the nature and origin of the bauxite ore, sizeable quantities of metallic and organic materials also go into the solution when the ore is digested with alkali. Because of successive recyclings the concentration of impurities in the liquor will gradually build up. The likely elements which are often found together with gallium in Bayer liquor are vanadium, iron, zinc, arsenic, antimony, molybdenum etc.

The gallium recovery process consists of gallium deposition onto mercury or sodium amalgam, dissolution of gallium amalgam to get sodium gallate solution and electrolysis of the same to give gallium metal. The amalgamation step and gallate electrolysis are critically inhibited by the presence of these impurities [1-7].

The aim is to study the effects of these metallic impurities on the reduction of gallate from alkaline solution and to interpret these results with particular reference to the recovery of gallium. The technique of linear stripping voltammetry on a rotating disc glassy carbon electrode (GCE) in a solution of alkaline gallate is adopted to get information on the above aspects.

EXPERIMENTAL

Linear stripping voltammetric studies were carried out using a conventional all glass electrolytic cell with provision for inlet and outlet for deaerating the solution with pure and dry nitrogen gas. A three electrode system consisting of a rotating teflon covered glassy carbon disc (6 mm dia) working electrode, a platinum counter electrode and a Hg/HgO in 1.0M NaOH reference electrode were used. The solutions were prepared from AR reagents and double distilled water. Sodium gallate solution of strength 4.3×10^{-3}M gallium in 0.5M NaOH was prepared by dissolving gallium oxide (JMC Grade-2) in alkali solution.

The gallium metal was deposited on GCE without and with the presence of impurities in solution at -2.0V for 2 minutes, which was then subjected to anodic sweep followed by cathodic sweep to complete the CV in the range - 2.0V to 0.0V. Before depositing gallium, the working electrode was polished with 3/0 and 4/0 grade emery paper, degreased with acetone and finally washed with twice distilled water. The following metallic ions viz: vanadium, iron, copper, zinc, and lead were added to the solution individually.

A Wenking (Model LB 75M) potentiostat coupled with a Wenking Scan Generator (Model VSG 72) was used for controlling the inputs. Tacussel rotating electrode set up (type EAD-10,000) was used for controlling the rotation rate of the working electrode. An X-Y recorder (Digitronic Model 2000 series) was used to record the i-E curves. All the potentials were expressed vs Hg/HgO in 1.00M NaOH. The measurements were carried out at 298 + 1 K.

RESULTS AND DISCUSSION

Linear stripping voltammetric experiments for the gallate systems On a rotating GCE, have been carried out in the presence and absence of metallic impurities in the solution. These experiments yielded well-defined and reproducible current potential curves.

Fig. 1A shows the typical cyclic voltammetric response of a sodium gallate solution having 4.3×10^{-3}M gallium in 0.5M NaOH. For comparison the stripping curve recorded under identical conditions for a solution containing no gallium in solution is given in Fig. 1B. Analysis of the stripping curve reveals that a well defined anodic peak for gallium dissolution is obtained at about -1.0V (cf. Fig. 1A). The typical influence of metallic impurities in solution on this anodic peak height throws light on their effect on gallium deposition.

The influence of the vanadium ion in solution on the anodic peak height is illustrated in Fig. 2. It is noted that the magnitude of the anodic peak currents are dependent on the concentration of the impurities. In the presence of vanadium an additional anodic dissolution peak appears at the potential region of -0.625V which corresponds to the accumulation of vanadium along with gallium at the time of deposition. If the concentration of vanadium in solution exceeds the limit of 15mgl^{-1}, the efficiency for deposition of
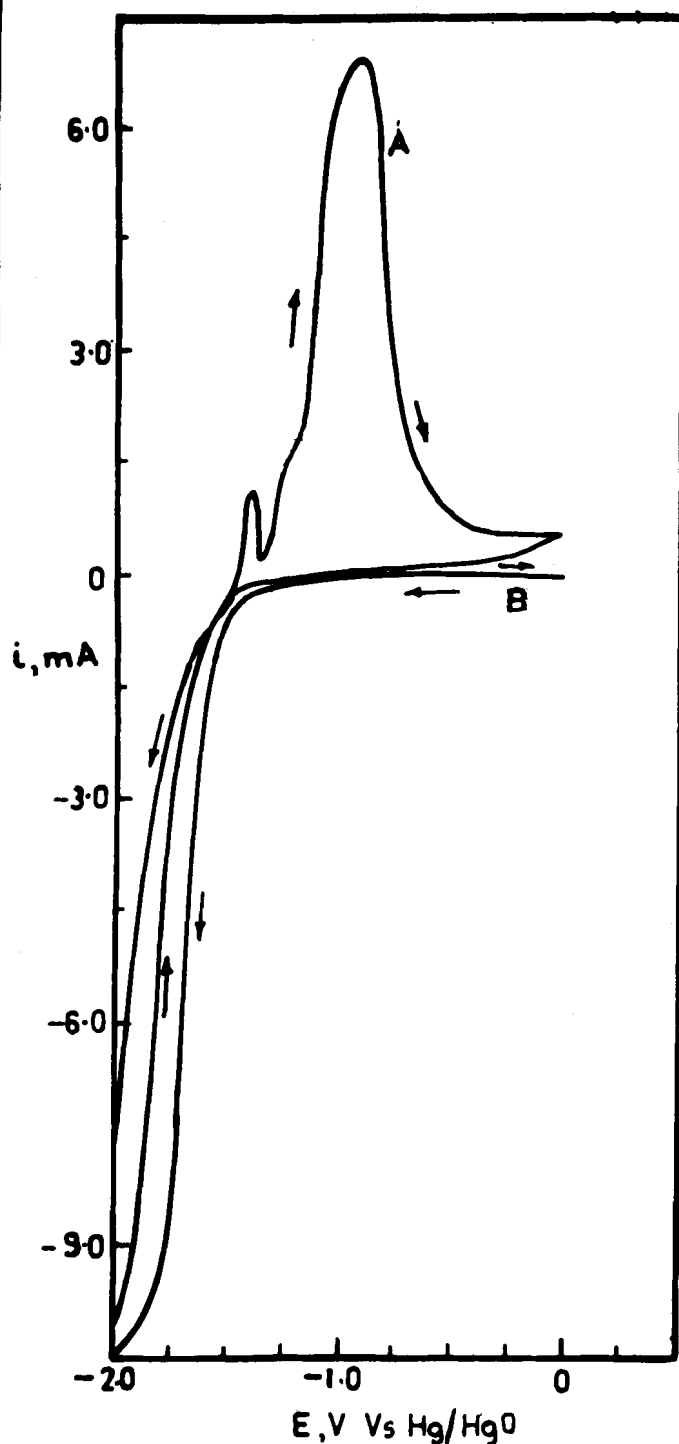
Fig. 1: (A) Cyclic voltammetric stripping curve on glassy carbon electrode after electrolysis at -2.0V for 2 minutes in 4.3 x 10⁻³M gallium in 0.5M NaOH. Scan rate 50 mVs⁻¹. Rotating rate 750m⁻¹. Range of potential sweep -2.0 to 0.0V. (B) As (A) but without gallium in solution
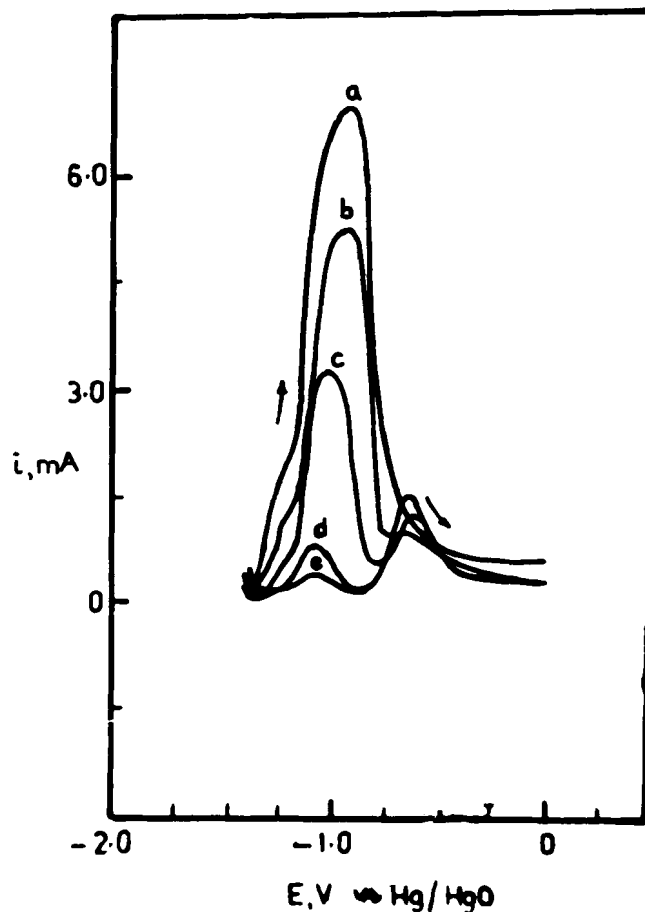

Fig.2: Effect of vanadium ion concentrations on the stripping curve obtained after electrolysis at -2.0V for 2 min in 4.3 x 10⁻³M gallium in 0.5M NaOH. Scan rate 50 mVs⁻¹. Rotation rate 750 m⁻¹ Range of potential sweep -2.0 to 0.0V. Vanadium ion concentrations: (a) 0 (b) 5 (c) 15 (d) 25 and (e) 50 mgl⁻¹

gallium drops rapidly to a minimum. Fig. 5 also clearly illustrates this observation. It is well known that gallium electrodeposition in alkaline media occurs in parallel with hydrogen evolution reaction. So the deleterious effect of vanadium above its critical level is attributed to the fact that its catalytic activity on hydrogen evolution reaction totally inhibits gallium deposition [7].

The typical influence of iron on the stripping curves obtained is shown in Fig.3. Progressive additions of iron (III) to the solution shows that above 10 mgl⁻¹ it precipitates out as hydroxide under the experimental conditions employed. The relative influence of iron on the deposition of gallium can be drawn from the magnitude of the anodic peak heights. It is reported that iron also catalyses the hydrogen evolution, the consequence being reduction in gallium deposition efficiency.

The influence of lead, copper and zinc on the anodic peak height

during redoping shows the n-type doping on the neutral polythiophene film. The increase in conductivity level, as seen in Fig.3, is not as high as that of p-type. This shows that during a single stage of doping the possibility of inserting the counter ion into the interior layers of the polymer film is slow and less effective as compared to the occurrence of the doping process along with polymerization observed in the case of p-type polythiophene synthesis. These curves further show the occurrence of compensation of p-type conductivity over by n-type conductivity which indicates the possibility of utilizing these materials in a variety of potential semiconductor device applications.

From these observation and the overall shape of the compensation curves as well as the fact that the doping can be removed electrochemically, it can be thought that the doping results from charge transfer reaction [10]. In the case of a p-type doping, charge transfer is believed to occur from polymer to acceptor (A) with the polymer chain acting as poly cation in the presence of A^- species as indicated below
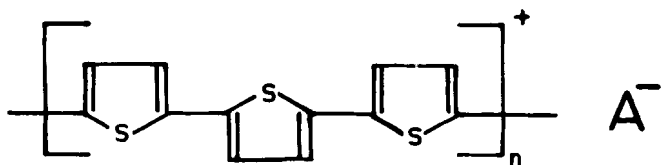
where $A^- = BF_4^-$ or ClO_4^- or AsF_6^-

For n-type doping, the polymer can act as a polyanion in the presence of donor (D) species and can be represented as follows:
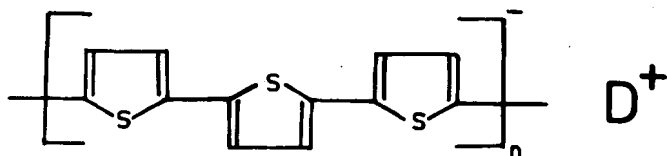
where $D^+ = (C_4H_9)_4N^+$ or Na^+ or K^+

The charge transfer in all these cases need not be complete. The resulting electron or hole on the polymer chain is bound to the D^+ or A^- ions by the coloumb potential, forming donor or acceptor states in the gap. At low levels, thermal activation out of the bound states results in carriers for transport along the polymer chain. Above certain level of doping, the bound states can be screened and the carriers are free to move along the polymer chains which can result in metallic behaviour of the polymer [11]. The compensation, as evident from the curve occurs through the formation of $(A^- D^+)$, leaving the polymer chain essentially as neutral and without electronic carriers.

CONCLUSION

An in situ electropolymerization offers a simple methodology to synthesise n-type, p-type and neutral polythio-phenes with the precise control of doping profile and thickness, besides the compensation of one type of conductivity over the other.

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