JOURNAL OF APPLIED ELECTROCHEMISTRY 18 (1988) 134–141

The electrodeposition of gallium from synthetic Bayer-process liquors

R. DORIN*, E. J. FRAZER

CSIRO Institute of Energy and Earth Resources, Division of Mineral Chemistry, PO Box 124, Port Melbourne, Victoria 3207, Australia

Received 28 May 1987; revised 24 July 1987

Gallium was electrodeposited from a synthetic Bayer solution comprising 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$. Hydrogen evolution occurred in parallel with gallium deposition, the latter process being in part controlled by mass transfer and in part by the electron transfer step. Combined coulometric and voltammetric measurements allowed estimation of a diffusion coefficient for Ga(III) of $3.6 \times 10^{-6}\,cm^2\,sec^{-1}$ at 40° C. The coulombic efficiency for gallium deposition was a function of current density, deposition time, electrode rotation rate, temperature and gallium concentration. Values of up to 11% were obtained on a copper electrode from a solution containing 3.2×10^{-3} M Ga(III). Heavy-metal impurities, such as iron and vanadium, usually found in these liquors, promote the hydrogen evolution reaction, completely inhibiting gallium production if present above certain critical concentrations.

1. Introduction

Since 1973, the world production of gallium has steadily increased with a corresponding decline in market price [1–4]. Recent technological developments in the electronics industries [5–7] suggest that the demand for gallium is set to increase substantially. Gallium is generally recovered as a by-product from Bayer-process liquors (sodium aluminate) due to the virtual non-existence of high-grade gallium ore bodies [8]. Processes also exist for its recovery from coal fly-ash and some zinc ores [9], but these sources are of little industrial importance. Gallium occurs as the oxide at levels of up to 0.1 wt% in bauxitic ores from which it is extracted into the recycled Bayer liquor. Here it attains an equilibrium concentration of about 200 p.p.m. [10, 11] depending on process conditions, the remainder being lost in both the precipitated alumina product and the red mud, which is the major waste-product. (A process has been proposed for the recovery of gallium from red mud [12].)

Conventional methods for the recovery of gallium from Bayer-process liquors always include a pre-concentration step. The Breteque process [13] involves the electroreduction of gallium into a mercury cathode. Because of strict environmental controls this method is now less attractive, though Abdul Kader *et al.* [14] have shown that mercury losses can be substantially reduced and gallium recovery enhanced by the use of a sodium amalgam cathode. The Beja process [15] involves carbonation of the liquor to concentrate the gallium; however, this results in a loss of sodium which must be made up if the liquor is to be recycled. A number of other procedures have been reported including solvent extraction [16–18], cementation with metallic aluminium or sodium [19, 20] and electrodeposition into alloy-forming substrates such as tin, lead, indium and zinc [21–23].

While commercial methods for gallium production from Bayer-process liquors have been reviewed [24–27], it seems that there has been no systematic evaluation of factors involved in the electrowinning of gallium from these solutions. Paciej [28, 29] demonstrated the advantage of improved mass transfer on the rate of gallium recovery using a microelectrode ensemble. Radvilla [30] using voltammetry, showed that the heavy metals, iron, molybdenum, vanadium and tungsten, normally found as impurities in Bayer liquors, inhibited gallium deposition into mercury, sodium amalgam and solid amalgam (Zn/Hg) cathodes, particularly the latter. He concluded that this inhibition resulted from the formation of thin oxide films whose effects were greatest on solid cathodes, where stirring of the surface to break up the film was not possible. However, Abdul Kader *et al.* [14] found that by using a 0.5% sodium amalgam cathode, vanadium (V), a major impurity in Bayer liquor, was reduced to the insoluble vanadium (III) form, enabling gallium deposition at current efficiencies up to 4%.

The aim of the present work was to identify the significant factors governing the deposition of gallium from sodium aluminate solutions and to determine the feasibility of a single-step electrorecovery process. Voltammetric and coulombic efficiency (*QE*) measurements were conducted in synthetic liquors to avoid interferences from impurities normally present in Bayer-process liquors. The variables considered were current density, electrode rotation rate, gallium concentration, temperature and deposition time. The effects of the common organic acids, formic, acetic, succinic and oxalic, both alone and in combination, at typical concentrations found in Australian Bayer liquors [31],

---

* To whom all correspondence should be addressed.

0021-891X/88 $03.00 + .12

were established. Also, the limiting levels of iron and vanadium for successful gallium electrodeposition were determined.

2. Experimental details

2.1. *Cell design and electrodes*

A conventional three-compartment electrochemical cell, with a working volume of ~ 150 ml, was modified for use in strong alkaline solutions. The glass frit which usually separates the auxiliary and working electrode compartments was replaced by a porous PTFE diaphragm (Zitex HV201-122, Chemplast Inc., New Jersey). This was secured over the end of a glass tube with a heat-shrink band (Man-O-Lok, Manostat Corp., New York) and the resulting assembly inserted into the auxiliary electrode compartment.

An Hg/HgO/1 M NaOH reference electrode was constructed, also with a porous polymeric diaphragm, and used for all potential measurements. The auxiliary electrode was a nickel flag of ~ 2 cm^2. The working electrode, which was usually copper (0.196 cm^2), was constructed by soldering a rod of the selected material into a brass holder which had been machined to fit the rotator (Beckman Model 1885). This assembly was encapsulated in Araldite epoxy LY556 (Ciba-Geigy), which was selected for its resistance to alkaline solutions. The base of the resulting cylinder was machined back and polished with 5 μm alumina paste giving a horizontal disc electrode. Other electrodes prepared in this way were manufactured from 316 stainless steel, lead (99.999%) and glassy carbon (Le Carbone); this latter material was sealed into the brass holder with silver epoxy (E-Solder 3021, Acme Adhesives).

2.2. *Solution preparation*

All solutions were prepared using doubly distilled water which was subsequently deionized through a Milli-Q System (Millipore Corporation, Mass.). Analytical-grade reagents were selected for their low iron content. Gallium sulphate (Fluka Puriss C grade) was used to prepare the gallium stock solution. Care must be taken in the selection of the gallium sulphate, since one source of this reagent was apparently contaminated by an impurity, e.g. a noble metal, which promoted hydrogen evolution at the expense of gallium deposition. Component concentrations were selected to reflect the approximate levels found in Australian Bayer liquors [31].

A synthetic liquor was prepared with the following composition: 4.5 M NaOH, 0.2 M Na_2CO_3, 1.7 M $Al(OH)_3$ and 0.3 M NaCl. It was used as the basis of all solutions tested. The sodium hydroxide (M & B Pronalys) was first dissolved in a small volume of water in a PTFE beaker and then the aluminium hydroxide (Baker Analyzed reagent) was added to the solution. It was necessary to maintain the temperature above 90°C to ensure ready dissolution of the $Al(OH)_3$. The solution was then further diluted with water to allow the dissolution of the remaining components (Na_2CO_3, NaCl (BDH AnalaR)). It was finally filtered under vacuum through a Millipore HVLP membrane and made up to the required volume with water. All solutions were deoxygenated by nitrogen sparging in the cell prior to electrochemical measurements.

As gallium sulphate is very hygroscopic, a stock solution of ~ 0.25 M Ga (III) was prepared and standardized by AAS. Approximately 2 ml of this solution were added to the cell to achieve the required concentration for the majority of the tests, 3.2×10^{-3} M. An iron (III) stock solution of ~ 0.01 M was prepared by dissolving $Fe_2(SO_4)_3$ in water. A vanadium (V) solution of ~ 0.3 M was prepared by dissolving V_2O_5 in a sodium hydroxide/sodium carbonate solution. A vanadium (IV) solution of ~ 1.2 M was prepared by the dissolution of vanadyl sulphate in water.

2.3. *Instrumentation*

All experiments were controlled by a PAR model 173 Potentiostat/Galvanostat fitted with a PAR model 179 Digital Coulometer. A Utah model 0150 sweep generator provided the potential scan for the voltammograms. These latter were recorded on a Hewlett-Packard model 7045A X-Y recorder. All other electrical data were recorded on a Yew model 3066, 3-pen Y-t recorder. The cell temperature was controlled by a Braun (Melsungen, W. Germany) Thermomix model 1420 immersion heater and circulation pump.

3. Results and discussion

3.1. *Voltammetry*

A general assessment of the gallium electrodeposition process was performed using voltammetry. The upper potential limit was set by the onset of oxidation of the substrate and the lower limit by the free evolution of hydrogen. The reproducibility of the electrode surface, its retention of the electrodeposited gallium and stripping characteristics were some of the factors which needed to be examined.

3.1.1. Choice of working electrode. Voltammograms were recorded on 316 stainless steel, lead, copper and glassy carbon electrodes in the synthetic liquor, firstly without, then with added gallium. The glassy carbon electrode was stable over the range from 0 to − 1.5 V,

Table 1. Stable potential limits for various substrates

Substrate	*Upper limit* (V) *at 1 mA cm*$^{-2}$	*Lower limits* (V)	
		at 1 mA cm^{-2}	*at 10 mA cm*$^{-2}$
316 Stainless	− 0.45	− 1.25	− 1.38 (− 1.61)*
Copper	− 0.50	− 1.30	− 1.47 (− 1.59)
Glassy carbon	0	− 1.40	− 1.50 (− 1.68)
Lead	− 0.80	− 1.39	− 1.52 (− 1.91)

* Figures in parentheses for solutions containing 3.2×10^{-3} M Ga (III).

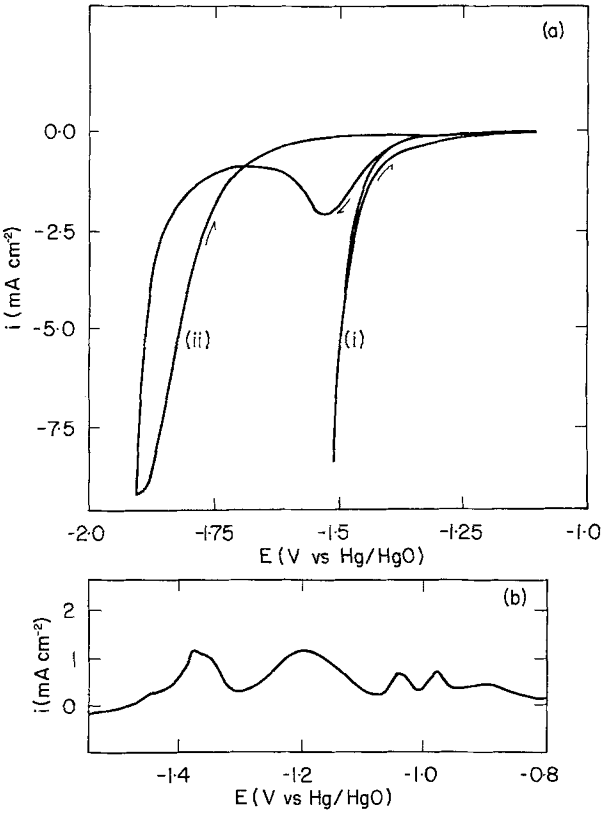

Fig. 1.(a) Voltammogram on lead electrode in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$ solution. Scan rate, 2 mV sec^{-1}; rotation rate, 20 sec^{-1}; temp, 40° C. (i) In absence of gallium; (ii) in presence of 3.2×10^{-3} M Ga(III). (b) Anodic stripping voltammogram on lead electrode after electrolysis at -1.90 V for 2 min in 3.2×10^{-3} M Ga(III) solution. Scan rate, 2 mV sec^{-1}; rotation rate, 20 sec^{-1}; temp, 40° C.

at which potential hydrogen was freely evolved. If the electrode was cycled between these limits, the hydrogen overpotential decreased, presumably as a result of a build-up of a solution impurity on the electrode surface (see section 3.4). The other electrodes had more restricted ranges of stability; the upper and lower potential limits are shown in Table 1.

When gallium was added to the solution (3.2×10^{-3} M), an increase in hydrogen overpotential was observed, apparently as a gallium film developed. This effect was most marked in the case of the lead electrode (see Fig. 1a) where the potential at a current density of 10 mA cm^{-2} decreased by 400 mV. From this observation one might assume that lead would be the most appropriate material for studying the electrodeposition of gallium. However, after deposition of gallium (and hydrogen) at -1.9 V for a 2 min period, the resultant stripping wave was complex and extended beyond the potential limit set by the oxidation of the lead (Fig. 1b). At high current densities (> 100 mA cm^{-2}) hydrogen evolution was sufficiently vigorous as to cause physical disintegration of the electrode surface, resulting in the formation of a fine grey suspension (presumably lead) throughout the solution. For these reasons, and also because of the difficulty of obtaining a reproducible surface, lead was not used for further tests.

The coulombic efficiency (*QE*) for gallium electrodeposition on 316 stainless steel, as measured by the ratio of coulombs of stripping current to plating current, was much less than that observed on a copper electrode under the same conditions. This was presumably due to its relatively low hydrogen overpotential compared to that of copper (see Table 1). While glassy carbon had a greater hydrogen overpotential than both stainless steel and copper, very low *QE*s were obtained; no gallium could be observed on the surface and this may be due to its partial adherence. The copper substrate has the advantage of alloy formation with the gallium [29, 32] which effectively lowers the gallium activity, allowing it to deposit at less negative potentials. Because of the above considerations, and since gallium had a single stripping peak within the stable potential range of copper, this substrate was selected for further experimentation. It was also noted that Varadharaj and Prabhakara Rao [33] had chosen a copper substrate (over stainless steel, graphite and silver) for studies in concentrated gallate solutions at 25° C because it formed a strongly adherent and stable gallium film.

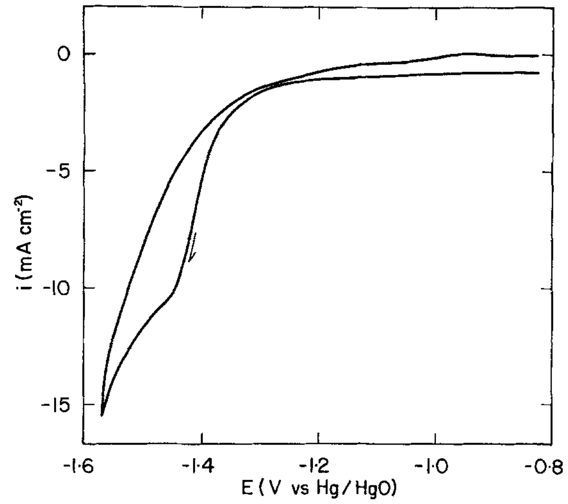

Fig. 2. Cathodic voltammogram on copper electrode in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2×10^{-3} M Ga(III) solution, showing gallium reduction wave partially obscured by hydrogen evolution. Scan rate, 2 mV sec^{-1}; rotation rate 20 sec^{-1}; temp, 40° C.

3.1.2. Gallium deposition wave. The gallium deposition wave was normally obscured by the hydrogen evolution process (see Fig. 2). The open circuit potential (OCP) for a gallium film on a copper substrate in 3.2×10^{-3} M Ga (III) was found to be -1.50 V. Observation of the stripping peak obtained on copper after constant potential plating at -1.8 V for 2 min (see Fig. 3), suggested that the reduction was, in part, mass-transfer-controlled up to a rotation rate of approximately 40 sec^{-1}. The stripping curves obtained by Varadharaj and Prabhakara Rao [34] when examining the effect of gallium concentration on its deposition into a hanging mercury drop electrode, are consistent with this view.

A gallium deposition wave for a synthetic Bayer solution containing 3.2×10^{-3} M Ga (III) was constructed using the following method. Gallium was plated at a series of fixed potentials for 2 min and the potential was then scanned in the positive direction to

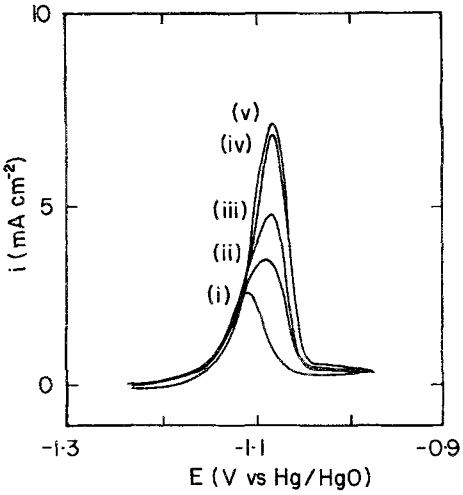

Fig. 3. Effect of rotation rate on the anodic stripping voltammogram on a copper electrode after electrolysis at -1.80 V for 2 min in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Scan rate, 2 mV sec^{-1}; temp, 40° C; rotation rate (sec^{-1}), (i) 5; (ii) 10; (iii) 20; (iv) 40; (v) 80.

produce a gallium stripping peak (see Fig. 4). Assuming a stripping efficiency of 100%, the average gallium partial current density at a given potential could be estimated from the charge defined by the peak. The resultant wave, which exhibited a limiting diffusion current of 2.85 mA cm^{-2}, is shown in Fig. 5. Using the Levich equation and a value of 2.6 × 10^{-2} cm^2 sec^{-1} for the kinematic viscosity (18% NaOH [35]), a diffusion coefficient for Ga (III) was calculated to be 3.6 × 10^{-6} cm^2 sec^{-1}. This is in agreement with the published figure of 3 × 10^{-6} cm^2 sec^{-1} in 7 M NaOH (room temperature assumed) [29].

3.2. *Coulombic efficiency determinations*

The *QE* for gallium electrodeposition was determined from the ratio of the stripping charge to the total coulombs passed. In the synthetic liquor, a *QE* of 6.7 ± 0.3% was observed under the following conditions, some of which were selected in view of the preliminary voltammetric experiments (see section 3.1): cathodic current density, 20 mA cm^{-2}; deposition time, ~42 min (to give 10 C); stripping potential, -0.7 V; electrode rotation rate, 20 sec^{-1}; temperature, 40°C (Ga m.p. 29.8°C); gallium concentration, 3.2 × 10^{-3} M. The effects of current density, deposition time, electrode rotation rate, gallium concentration and temperature on *QE* were individually assessed over limited ranges while holding the remaining variables constant (see following sections).

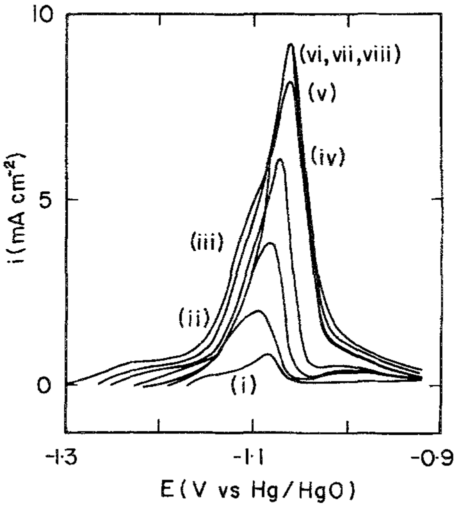

Fig. 4. Effect of the electrolysis potential (held for 2 min) on the anodic stripping voltammmogram on a copper electrode in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Scan rate, 2 mV sec^{-1}; temp, 40° C; electrode rotation rate, 20 sec^{-1}; potentials (V), (i) -1.50; (ii) -1.60; (iii) -1.65; (iv) -1.70; (v) -1.75; (vi) -1.80; (vii) -1.85; (viii) -1.90.

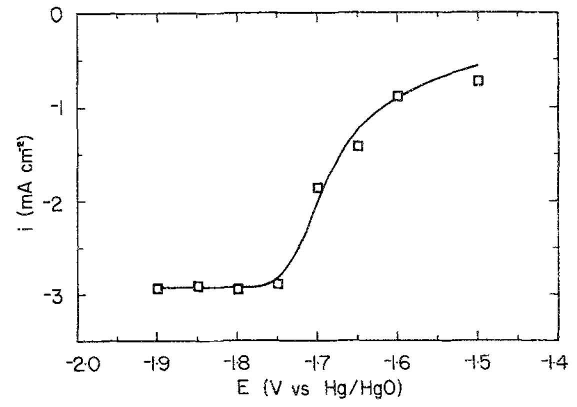

Fig. 5. Derived gallium reduction wave in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Temp, 40° C; rotation rate, 20 sec^{-1}.

3.2.1. *Effect of current density.*

A maximum *QE* of 8.6% was observed (see Fig. 6) at a current density of ~ 10 mA cm^{-2} which corresponds to a potential of -1.62 V, some 120 mV more negative than the gallium OCP (see section 3.1.2). At higher current densities a decrease in *QE* was observed, suggesting a relative increase in the rate of hydrogen evolution. The maximum *QE* observed here is of the same order as that expected from the derived gallium wave (Fig. 5), which shows a gallium partial current density of ~ 1 mA cm^{-2} at about -1.6 V (i.e., a *QE* of ~ 10%). Current densities below 10 mA cm^{-2} were insufficient to force the electrode potential beyond the gallium OCP (see also section 3.4.2).

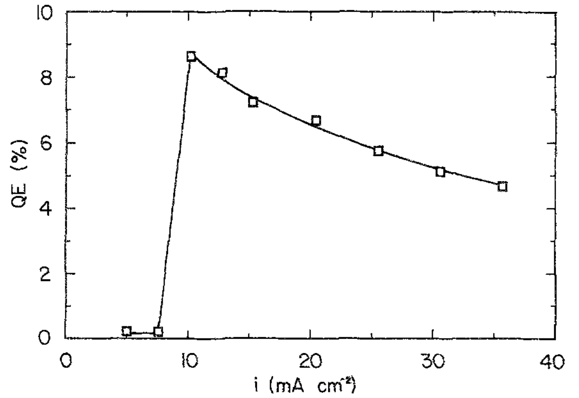

Fig. 6. Effect of current density on *QE* in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Temp, 40° C; deposition time, ~42 min; rotation rate, 20 sec^{-1}.

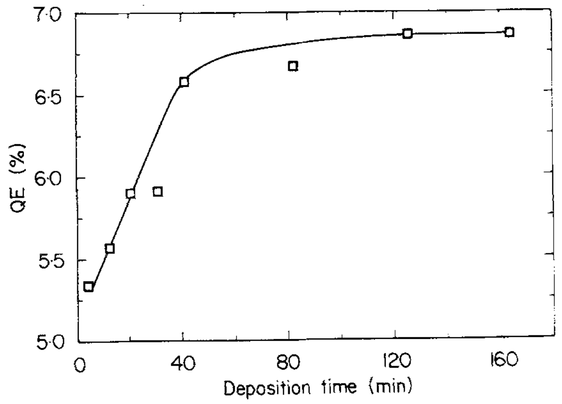

Fig. 7. Effect of deposition time on QE in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Temp, 40° C; rotation rate, 20 sec^{-1}; current density, 20 mA cm^{-2}.

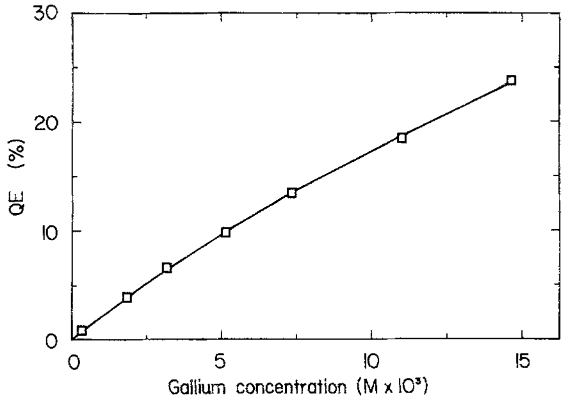

Fig. 9. Effect of gallium concentration on QE in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$ solution. Temp, 40° C; deposition time, ~42 min; current density, 20 mA cm^{-2}; rotation rate, 20 sec^{-1}.

3.2.2. *Effect of deposition time.* The QE gradually increased with increasing deposition time (see Fig. 7) which presumably reflects the increasing hydrogen overpotential as the surface composition changes from copper through copper–gallium alloy to pure gallium. Also, with extended deposition times, the contribution to the overall QE from the initial stages of gallium surface development becomes increasingly less significant and the QE approaches a constant value.

3.2.3. *Effect of electrode rotation rate.* The variation of QE with electrode rotation rate over a limited range is shown in Fig. 8. This curve has the shape expected for a reaction controlled by mixed kinetics [36]. Measurements at less than 4 sec^{-1} were unreliable because of the retention of hydrogen gas bubbles on the electrode which reduced the available surface area. At high rotation rates, above 40 sec^{-1}, the hydrogen evolution reaction is catalysed by the increased mass transfer of trace impurities to the electrode surface (see section 3.4.2). As a result, the potential was increased above the gallium OCP preventing its deposition.

3.2.4. *Effect of gallium concentration.* Fig. 9 shows the effect of gallium concentration on QE; at a constant electrode rotation rate, increasing gallium concentration steadily increases QE. The non-linearity of the curve is further indication of mixed kinetics governing the electrodeposition process.

3.2.5. *Effect of temperature.* The effect of temperature is shown in Fig. 10 which displays an almost linear increase in QE up to ~ 50° C. This behaviour is consistent with a partly activation-controlled mechanism, although the effect of increasing temperature on the competing process (hydrogen evolution) and on the rate of impurity deposition is unknown.

3.2.6. *QE enhancement under selected conditions.* It was shown above that a QE of ~6.7% was possible under a set of non-optimized electrolysis conditions. The observed variations of QE with current density, deposition time, electrode rotation rate and temperature (sections 3.2.1–5) suggested that the above figure could be substantially improved by careful selection of electrolysis conditions. Hence the QE was determined under the near-optimum values identified, *viz.* 10 mA cm^{-2}, 42 min, 36 sec^{-1}, and 50° C. A QE of 11.0% was obtained which is virtually equivalent to the value calculated (10.7%) assuming additivity of the individual contributions to QE. Therefore, it appears that under these conditions, there are no significant interactions between the electrolysis variables.

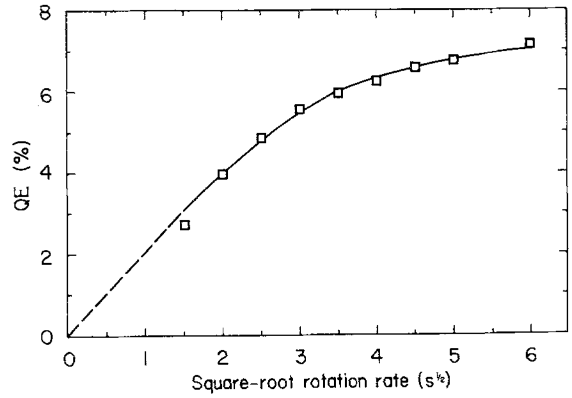

Fig. 8. Effect of electrode rotation rate on QE in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Temp, 40° C; deposition time, ~42 min; current density, 20 mA cm^{-2}.

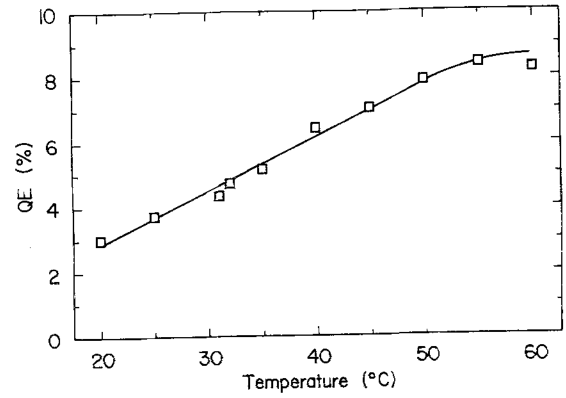

Fig. 10. Effect of temperature on QE in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Deposition time, ~42 min; current density, 20 mA cm^{-2}; rotation rate, 20 sec^{-1}.

3.3. *Effect of organic solution components*

Bayer-process liquor contains a wide variety of organics formed by the decomposition of cellulose and lignine which occur in the bauxite. The effect on *QE* of the most common of these decomposition products was examined.

Synthetic liquors were prepared with individual additions of the following organic salts: sodium formate (0.10 M), sodium acetate (0.20 M), sodium oxalate (0.03 M) and sodium succinate (0.02 M). A further solution was prepared containing all these additives. While additions of the individual organic salts did not affect *QE* significantly, the combination of all four reduced the *QE* from 6.7 to 5.1% suggesting some deleterious synergism.

3.4. *Effect of inorganic solution components and impurities*

Preliminary experiments established that sodium carbonate and sodium chloride had no measurable effect on *QE* and these materials were incorporated into the synthetic Bayer liquor (see section 2.2). The addition of orthophosphoric acid to the solution, at a typical concentration of 88 p.p.m. P [31], had no significant effect on *QE* and the acid was not added to any other solutions. Two impurities, iron and vanadium, known to be deleterious in gallium electrodeposition from Bayer liquors [14, 20, 37], were evaluated here. Commercial liquors may also contain other potentially deleterious impurities such as arsenic, molybdenum, tin and tungsten.

3.4.1. Vanadium (IV) and (V). Progressive additions of vanadium (V) to the cell under the standard test conditions showed that there was a critical concentration level of 30 p.p.m. (see Fig. 11), beyond which the *QE* dropped effectively to zero. Above 30 p.p.m. the electrode potential increased to − 1.35 V (which is 150 mV less negative than the gallium OCP) indicating catalysis of the hydrogen evolution reaction. The deleterious effect of vanadium (V) on *QE* was not significantly altered by changing the electrode rotation rate. The critical level identified above is only marginally lower than the 50 p.p.m. 'threshold' reported by Abdul Kader *et al.* [37] on a sodium amalgam cathode. If the copper electrode was pre-plated with gallium, the vanadium concentration could be increased to ~ 60 p.p.m. before the *QE* was affected.

Vanadium (IV) also inhibited gallium deposition when introduced at vanadium levels normally encountered in practice. Energy dispersive X-ray spectrometry (EDX) analysis of the electrode surface, in a scanning electron microscope, revealed the presence of a trace of vanadium. While its oxidation state is unknown, the formation of an insoluble V(III) compound has been reported [14] under reducing conditions.

3.4.2. Iron (III). The deposition of gallium was found to be very sensitive to the iron concentration in solution. The synthetic Bayer liquors always had a background concentration of ~ 2 p.p.m. Fe, but this was not sufficient to prevent gallium production under the standard deposition conditions. However, when the current density was reduced to below 10 mA cm^{-2}, a bright film (iron), which was deposited at up to 300 mV more positive than the gallium OCP, was observed and the evolution of hydrogen was promoted. Examination of the electrode surface using EDX confirmed the presence of iron and the total absence of gallium.

Progressive additions of iron (III) to the solution showed that, under the standard test conditions (20 mA cm^{-2}), gallium continued to be plated without interference up to ~ 4 p.p.m. Fe; above this value, the *QE* dropped rapidly to zero (see Fig. 12). Reducing the electrode rotation rate from 20 to 9 sec^{-1}, while just above the critical iron concentration (4 p.p.m.), did permit the deposition of gallium, albeit at a reduced *QE* (4.1%), further demonstrating the importance of mass-transfer rate (see section 3.2.3).

3.5. *Tests on commercial Bayer liquor*

A sample of commercial Bayer liquor was electrolysed

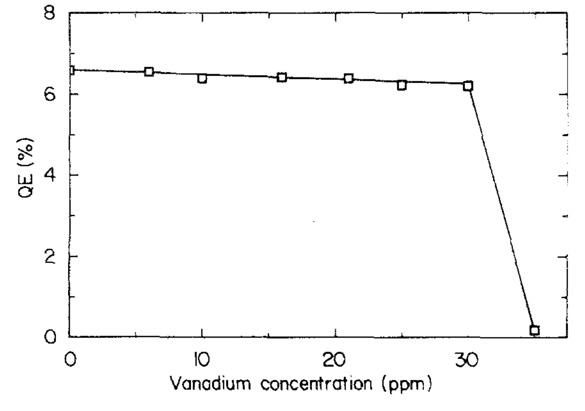

Fig. 11. Effect of vanadium (V) concentration on *QE* in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Temp, 40° C; deposition time, ~ 42 min; current density, 20 mA cm^{-2}; rotation rate, 20 sec^{-1}.

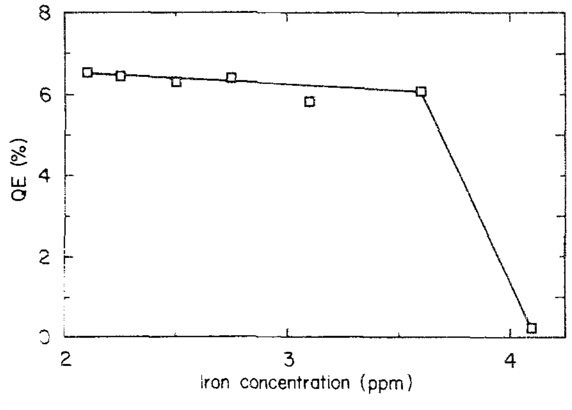

Fig. 12. Effect of iron (III) concentration on *QE* in 4.5 M NaOH/0.2 M Na_2CO_3/0.3 M NaCl/1.7 M $Al(OH)_3$/3.2 × 10^{-3} M Ga(III) solution. Temp, 40° C; deposition time, ~ 42 min; current density, 20 mA cm^{-2}; rotation rate, 20 sec^{-1}.

using a copper cathode under the standard test conditions (and also at 50° C). The electrode potential observed was 300 mV more positive than the gallium OCP and EDX analysis of the electrode surface following electrolysis revealed no gallium, only traces of vanadium. This liquor contained ~ 150 p.p.m. V, and in view of the foregoing observations, this result was not unexpected.

4. Conclusions

The electrodeposition of gallium from sodium aluminate solutions occurs in parallel with the hydrogen evolution reaction. Some materials which have high hydrogen overpotentials, such as lead and glassy carbon, were found to be unsuitable substrates for studying gallium electrodeposition. Copper was found to be the most suitable material as it was readily 'wetted' by the depositing gallium with which it forms alloys. The resulting gallium film electrode showed an enhanced hydrogen overpotential and the *QE* was improved relative to that obtained prior to the development of the film.

The *QE* was found to be a function of current density, deposition time, electrode rotation rate, temperature and gallium concentration. The results obtained were consistent with a process which is in part controlled by mass transfer and in part by the electron transfer step. A *QE* of up to 11% could be obtained in pure solutions under selected conditions; further improvement may be possible using statistical optimization techniques. This figure is somewhat better than that obtained by Breteque [10] and Abdul Kader *et al.* [14] who both reported around 5% on mercury cathodes, admittedly in the presence of impurities. The benefit of a gallium preconcentration step on the efficiency of its recovery has been demonstrated, a five-fold increase in gallium concentration yielding an almost equivalent improvement in *QE*.

A single-step gallium electrorecovery process from Bayer-process liquors does not seem feasible without the prior removal of certain heavy-metal impurities down to low levels. It was confirmed that iron and vanadium catalysed the hydrogen evolution reaction and when above critical levels, completely inhibited gallium production. Fortunately the concentration of iron in Bayer liquor is typically lower than the estimated critical level and therefore, although synergistic effects have not been considered, iron may not be a problem in practice. However, vanadium levels of up to 400 p.p.m. are normally present and would need to be substantially reduced; several methods for its removal have been reported including slow cooling [27]; cementation with sodium [14, 20] and aluminium [19, 21]; addition of sodium hyposulphite [23, 38]; electrolysis employing a low-melting liquid alloy cathode [39] and precipitation by seeding [40]. It may also be necessary to reduce the concentration of the organic solution components, for which a method based on the addition of magnesium sulphate has been reported [41].

Acknowledgements

The authors would like to thank T. Biegler, J. H. Canterford and S. Fletcher for discussions and advice. Also, thanks are due to H. Gardner, K. J. Cathro, D. A. J. Rand, and M. D. Horne for loan of equipment. Analytical work was carried out by P. R. Strode and the SEM was operated by C. M. MacRae and P. Rummel. Technical assistance was provided by R. A. Pillig, S. J. Lentini and H. Gidney.

References

[1] F. D. Rosi, *Materials and Society* **4** (1980) 349.
[2] L. Baumgardner, in 'Minerals Yearbook', Vol. 1, United States Bureau of Mines, Washington (1983) p.349.
[3] D. A. Kramer, *ibid.* (1984) p.387.
[4] B. Petkof, in 'Mineral Facts and Problems', Bulletin 675, United States Bureau of Mines, Washington (1985).
[5] F. E. Katrak and J. C. Agarwal, *J. Metals* **33** (1981) 33.
[6] S. Zwerdling, K. L. Wang and Y. C. M. Yeh, *J. Solar Energy Eng.* **105** (1983) 237.
[7] C. L. Cohen, *Electronics* **10**(2) (1986) 17.
[8] I. A. Sheka, I. S. Chaus and T. T. Mityureva, in 'The Chemistry of Gallium', Elsevier, Amsterdam (1966) p.8.
[9] T. C. Wilder and F. E. Katrak, in 'Hydrometallurgy of Copper, Its Byproducts and Rarer Metals', Proc. Dallas Symp. Feb. 1982, edited by L. A. Haas and D. R. Weir, SME/AIME, New York (1983) p.51.
[10] P. de la Breteque, *J. Metals* **8** (1956) 1528.
[11] J. A. M. Abdul Khader, A. Varadaraj, G. N. Srinivasan and R. Srinivasan, *Chem. Ind. Dev.* **8**(1) (1974) 22.
[12] Z. Soljic and V. Marajanovic, *Chim. Anal.* **52** (1970) 285.
[13] P. de la Breteque, US Patent 2 793 179 (1957).
[14] J. A. M. Abdul Kader, A. Varadaraj, G. N. Srinivasan and R. Srinivasan, *Trans. SAEST* **10** (1975) 249.
[15] M. Beja, US Patent 2 574 008 (1951).
[16] J. Helgorsky and A. Leveque, German Offen. 2 743 475 (1978); *Chem. Abstr.* **89** (1978) 28421.
[17] A. Leveque and J. Helgorsky, in 'Proceedings of the International Solvent Extraction Conference, Vol. 2', Toronto, Sept. 1977, CIM Toronto (1979) p.439.
[18] V. I. Bukin, P. V. Zhukovskii and A. M. Reznik, *Tsvet. Met. (Engl.)* **25**(8) (1984) 60.
[19] W. Westwood, J. J. MacGregor and J. B. Payne, US Patent 4 029 499 (1977).
[20] J. A. M. Abdul Kader, A. Varadaraj, G. N. Srinivasan and R. Srinivasan, *Indian J. Tech.* **13** (1975) 139.
[21] G. M. Phatak and K. Gangadharan, in 'Proceedings of the Symposium of Fundamental and Applied Electrochemistry', edited by K. M. Joshi and M. K. Totlani, Soc. Adv. Electrochem. Sci. Technol., Bombay (1982) p.156.
[22] C. G. Honey, S. L. Jones and S. W. Summers, British Patent 1 436 260 (1976).
[23] G. M. Rubinshtein, US Patent 4 368 108 (1983).
[24] L. K. Hudson, *J. Metals* **17** (1965) 948.
[25] Kirk-Othmer, 'Encylopaedia of Chemical Technology', 3rd. edn., Vol. 11, John Wiley & Sons, New York (1980) p.604.
[26] J. A. M. Abdul Kader, A. Varadharaj, G. N. Srinivasan, R. Raman and R. Srinivasan, *Trans. Indian Inst. Met.* **35** (1982) 276.
[27] O. Klugg and S. Zsindely, *Proc. Res. Inst. Nonferr. Met.* **9** (1971) 261.
[28] R. C. Paciej, MSc Thesis, Univ. Virginia, USA (1982).
[29] R. C. Paciej, G. L. Cahen Jr., G. E. Stoner and E. Gileadi, *J. Electrochem. Soc.* **132** (1985) 1307.
[30] P. R. Radvilla, *Chimia* **37** (1983) 15.
[31] L. D. Jayaweera, PhD Thesis, Univ. New South Wales, Australia (1981).
[32] M. Hansen, in 'Constitution of Binary Alloys', 2nd. edn., McGraw-Hill, New York (1958) p.582.
[33] A. Varadharaj and G. Prabhakara Rao, *J. Electroanal. Chem.* **138** (1982) 189.
[34] A. Varadharaj and G. Prabhakara Rao, *J. Appl. Electrochem.* **16** (1986) 929.

[35] Handbook of Chemistry and Physics, 55th. edn. (edited by R. C. Weast), C.R.C. Press, Ohio (1974/5) p.D227.

[36] F. Opekar and P. Beran, *J. Electroanal. Chem.* **69** (1976) 1.

[37] J. A. M. Abdul Kader, A. Varadharaj, G. N. Srinivasan and R. Srinivasan, in 'Proceedings of the 12th Seminar on Electrochemistry', Karaikudi, India (1972) p.43.

[38] Chuo Tatemono Co. Ltd., Fr. Demande 2 021 126 (1970); *Chem. Abstr.* **74** (1971) 144925.

[39] G. Sinka, M. Miskei, F. Toth, L. Revesz and M. Schlegel, US Patent 4 362 606 (1982).

[40] Sumitomo Chemical Co., Australian Patent Appl. 88741/82 (1982).

[41] H. H. Pohland and A. J. Tielens, in 'Light Metals' (edited by E. M. Adkins), The Metallurgical Society of AIME, Pennsylvania (1983) p.211.