

The electrodeposition of chromium from chromium(III) solutions — a study using microelectrodes

J. N. HOWARTH, D. PLETCHER

Department of Chemistry, The University, Southampton SO9 5NH, UK

Received 2 December 1987; revised 22 January 1988

Potential sweep and pulse experiments at a carbon microdisc electrode (radius $4\ \mu\text{m}$) have been used to investigate chromium plating from aqueous solutions of chromic ions containing sulphate or thiocyanate ions and buffered at pH 3.3. While chromium deposition occurs in many media, it is shown that the plating reaction is always in competition with other cathodic reactions including hydrogen evolution. This leads to loss in current efficiency and, in some circumstances, to precipitation of chromic hydroxide on the cathode and, hence, contamination of the metal. In addition, it is demonstrated that the chromium(III) exists in solution as mixtures of complexes, not all of which are electroactive within the accessible potential range. Hence the investigation confirms that the quality of electroplates will vary strongly with the choice of medium. A commercial chromium(III) plating bath, Envirochrome, has also been studied and it is concluded that its properties are superior to simple sulphate or thiocyanate solutions.

1. Introduction

Chromium metal is widely electroplated onto consumer goods and engineering components in order to improve appearance, corrosion resistance and/or wear of surfaces. Traditionally, the metal is plated from an electrolyte bath containing Cr(VI) and sulphuric acid and, indeed, such baths remain dominant within commercial technology [1-3]. It is, however, universally recognized that these Cr(VI) baths have several shortcomings; chromium(VI) is extremely toxic, expensive treatment of wash waters prior to disposal is essential, the current efficiency of the plating process is very low and the number of plates failing to meet specification is uncomfortably high.

These problems have led to an extensive search for a viable electroplating bath based on a chromium(III) salt. The design of such a bath is made difficult by: (a) the chemistry of Cr(III) which is substitution inert, slow to reduce and readily hydrolysed; (b) the negative value of the formal potential of the Cr(III)/Cr couple in most aqueous media; (c) the moderate catalytic activity of chromium for the H_2 evolution reaction. Indeed, for many years it was often stated that deposition of metal from Cr(III) solutions was impossible. More recently, the patent and technical literature [4-27] have claimed deposition from several baths and one company, W. Canning Ltd. now markets the Envirochrome process, a bath for decorative plating based on Cr(III) [28, 29].

In the development of the Envirochrome system by Barclay and co-workers [4-18, 25], the basic concept appears to be that the bath should contain: (a) a source of Cr(III); (b) a buffer of high capacity to hold the bulk pH in the range 3-4; (c) a catalyst for the reduction of Cr(III), for example thiocyanate [30, 31];

(d) a complexant, i.e. a ligand with a stability constant high enough to stabilize the Cr(III) to hydrolysis but not so high as to shift the formal potential of the Cr(III)/Cr couple to too negative a value. It is also advantageous if the ligand can act as an 'intimate buffer' when released in the plating reaction, i.e. act as a buffer in the critical layer at the electrode surface most prone to pH swing during competing hydrogen evolution. A typical ligand would be an amino acid or a hydroxy carboxylic acid; (e) additives to improve the characteristics of the electrodeposit, e.g. thiourea, surfactant. In some formulations one species seems to perform more than one of these functions.

Most knowledge of the mechanisms of chromium deposition reactions results from extensive electroplating experiments and relatively little use has been made of modern electroanalytical techniques. This is, perhaps, largely because of the high rate of H_2 evolution which normally accompanies Cr deposition. Indeed we are aware of one such study [32] of Cr(III) and only a few of Cr(VI) baths [33-36]. In this paper, we apply linear potential sweep and potential step techniques at C ultramicroelectrodes to the investigation of Cr deposition from some Cr(III) solutions. The advantages of the ultramicroelectrodes [37] of particular importance to these experiments are: (i) to minimize distortion of the data by uncompensated iR drop — Cr deposition requires a high current density; (ii) the response due to mass transport-limited processes, e.g. Cr deposition, is enhanced relative to that for kinetically controlled reactions, e.g. water reduction; (iii) charging currents are much reduced. Our group has previously used such electrodes in the study of metal deposition — lithium [38, 39], magnesium [40] and aluminium [41] — from non-aqueous solvents.

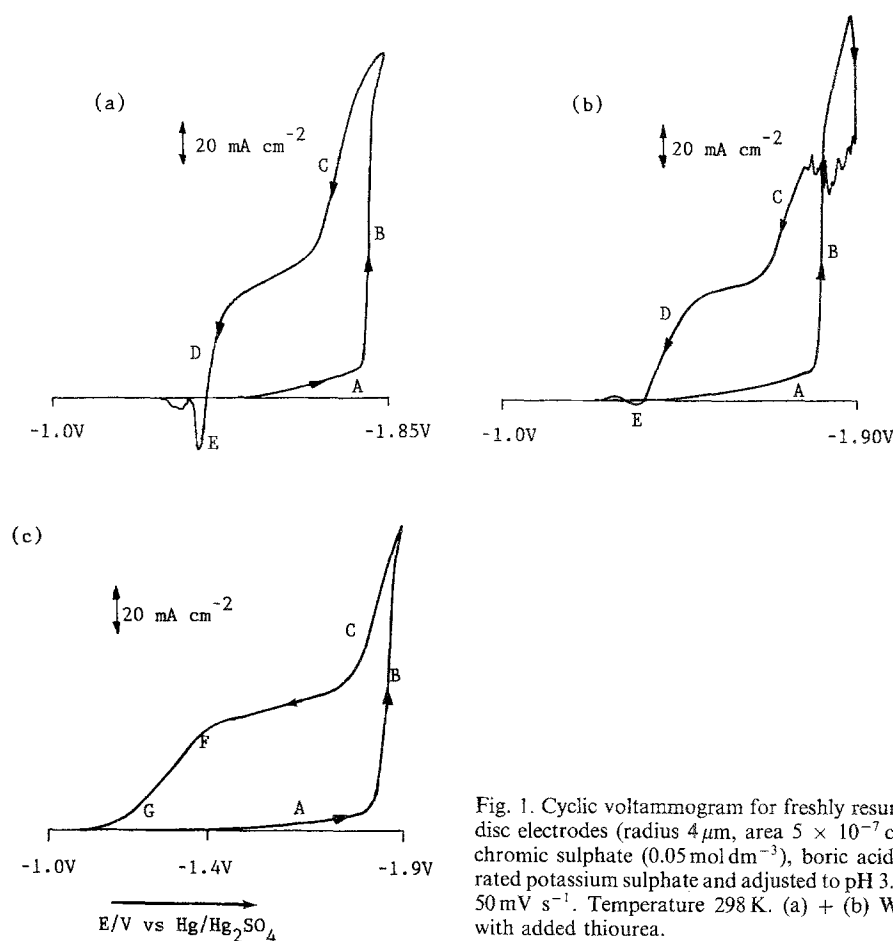


Fig. 1. Cyclic voltammogram for freshly resurfaced carbon microdisc electrodes (radius $4\ \mu\text{m}$, area $5 \times 10^{-7}\ \text{cm}^2$) in a solution of chromic sulphate ($0.05\ \text{mol dm}^{-3}$), boric acid ($1\ \text{mol dm}^{-3}$), saturated potassium sulphate and adjusted to pH 3.3. Potential scan rate $50\ \text{mV s}^{-1}$. Temperature $298\ \text{K}$. (a) + (b) Without thiourea, (c) with added thiourea.

2. Experimental details

The experiments were all carried out with a two-electrode cell. The carbon microdisc electrodes (radius $4\ \mu\text{m}$, area $5 \times 10^{-7}\ \text{cm}^2$) were prepared by sealing carbon fibres into soda glass; electrical contact was made via Hg to a Ni wire. The fibre protruding from the glass was cut to expose the disc which was ground flat with $12\ \mu\text{m}$ emery paper and polished with $3\ \mu\text{m}$ Al_2O_3 /water paste. The reference/counter electrode was a home prepared $\text{Hg}|\text{Hg}_2\text{SO}_4|\text{sat. K}_2\text{SO}_4$ electrode separated from the working solution by a glass sinter. Solutions were deoxygenated thoroughly with a stream of N_2 . The potential of the microelectrode was programmed with a Hi-Tek Function Generator, model PPR1 and the current flowing through the cell was amplified with a home-built amplifier capable of operating in the current range 10^{-9} – 10^{-4} A. The amplifier output was displayed on a Farnell xy recorder or via a Gould Digital Oscilloscope, OS4100, to the recorder. The plating baths were prepared with water from a Millipore-Milliro system and the purest chemicals available. The sulphate and thiocyanate solutions were prepared by dissolving the appropriate weights of chromic sulphate, boric acid, potassium sulphate (and sodium thiocyanate) and refluxing for 6 h. After cooling, 10% NaOH was added with vigorous stirring to pH 3.3. The Envirochrome bath was prepared from ingredients supplied by W. Cannings Materials Ltd and formulated according to their instructions [29].

The base salts (130 g) were dissolved in the liquid concentrate ($50\ \text{cm}^3$) and water was added to $450\ \text{cm}^3$; the solution was then refluxed for 6 h. After cooling, the initial additive ($5\ \text{cm}^3$) and wetting agent ($1.5\ \text{cm}^3$) were added and the pH adjusted to pH 3.3 by addition of 10% NaOH with vigorous stirring. The volume was made up to $500\ \text{cm}^3$. The Cr(III) content of this solution was $0.09\ \text{mol dm}^{-3}$ as determined by dilution and atomic absorption spectroscopy.

3. Results

3.1. Chromic sulphate solutions

In the first series of experiments, the bath was a buffered sulphate medium and there was no deliberate addition of further complexing ligands. The solution was chromic ion ($0.1\ \text{mol dm}^{-3}$) – $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ – in a borate buffer ($1\ \text{mol dm}^{-3}$, pH 3.3) saturated with potassium sulphate.

Figure 1a shows a cyclic voltammogram for a freshly resurfaced carbon disc microelectrode, radius $4\ \mu\text{m}$, in this solution. The potential limits are -1.0 to $-1.85\ \text{V}$ vs a $\text{Hg}|\text{Hg}_2\text{SO}_4$ reference electrode and the scan rate $50\ \text{mV s}^{-1}$. On the forward sweep, only a low cathodic current, labelled A, is observed (probably due to H^+ reduction on the carbon surface) until the potential reaches $-1.79\ \text{V}$. Thereafter the current increases very rapidly and tends to a limiting value at about $200\ \text{mA cm}^{-2}$. The back sweep is very different and shows two

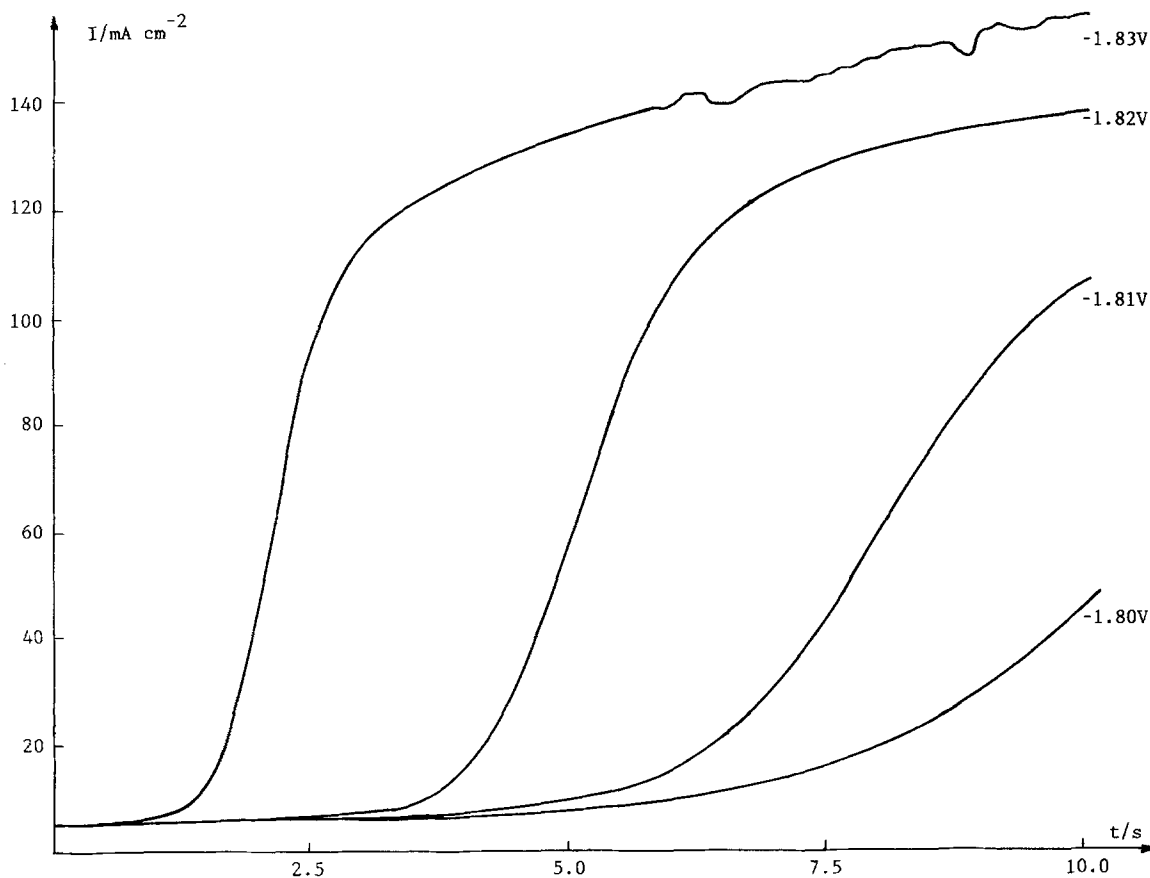


Fig. 2. $I-t$ transients in response to potential steps from 0 V vs Hg/Hg₂SO₄ to the values shown. Resurfaced carbon microdisc electrodes (radius 4 μ m) in a solution of chromic sulphate (0.05 mol dm⁻³), boric acid (1 mol dm⁻³), saturated potassium sulphate and adjusted to pH 3.3. Temperature 298 K.

cathodic processes with $E_{1/2} = -1.73$ and -1.42 V, labelled C and D, respectively, as well as an anodic peak, E, at -1.38 V. Such strong hysteresis shows conclusively that process B involves a change in the electrode surface. Moreover the strong take-off of the current at -1.78 V on the forward scan is quite characteristic of a phase nucleation and growth process. It will be argued below that: (a) wave C is for the deposition of Cr; (b) process D is for a reduction promoted by the presence of a clean Cr surface, e.g. H⁺ reduction; (c) therefore wave B arises both from Cr deposition and also reactions occurring on Cr but not C surfaces; (d) peak E is for the corrosion and passivation of Cr.

In the experiment of Fig. 1b, the negative potential limit has been extended to -1.90 V. It can be seen that, in fact, process B does not give a wave with a well-defined plateau. Rather the response goes through a sharp peak at -1.87 V, thereafter the current falling rapidly. On the reverse scan, the plateau region of wave C shows a rather erratic response and both wave C and peak E are of much diminished size. Such changes in the voltammogram could arise if precipitation of Cr(OH)₃ or similar basic Cr(III) salt occurs at potentials negative to the current peak and causes partial passivation of the Cr surface. Figure 1(c) shows the response from the same experiment but after the addition of a low concentration of thiourea to the solution. It can be seen that on the forward

scan, the presence of the thiourea inhibits the phase growth process and the current rise does not occur until -1.83 V. Hence the feature B and the passivation phenomena are shifted to more negative potentials. On the reverse sweep, wave C is again observed but there is no evidence of an anodic peak implying that the Cr corrosion is inhibited. Moreover, cathodic process D appears to be replaced by two waves F and G at less negative potentials. These last two observations are probably related. The formation of a passivating film on the deposited Cr at -1.38 V will inhibit all electron transfer reactions; hence the reactions leading to waves F and G will stop as soon as the corrosion film forms on the chromium and the stopping of reactions F and G will be seen as a single wave, D, just negative to peak E in the absence of thiourea. The addition of a few drops of a solution of the surfactant, Triton X-100, to the solution did not lead to any further changes in cyclic voltammogram.

Figure 2 reports the $I-t$ transients in response to potential steps from 0.0 V to the potentials shown; the medium is the sulphate solution without thiourea and the electrode is a freshly resurfaced C microdisc. At each of the four potentials, there is an initial delay and then the current increases smoothly from a low value towards a limiting current. The timescale of the transients decreases as the potential is made more negative and an analysis of the first part of the rising portions show they give good linear $I^{1/3}$ vs t plots. Hence a

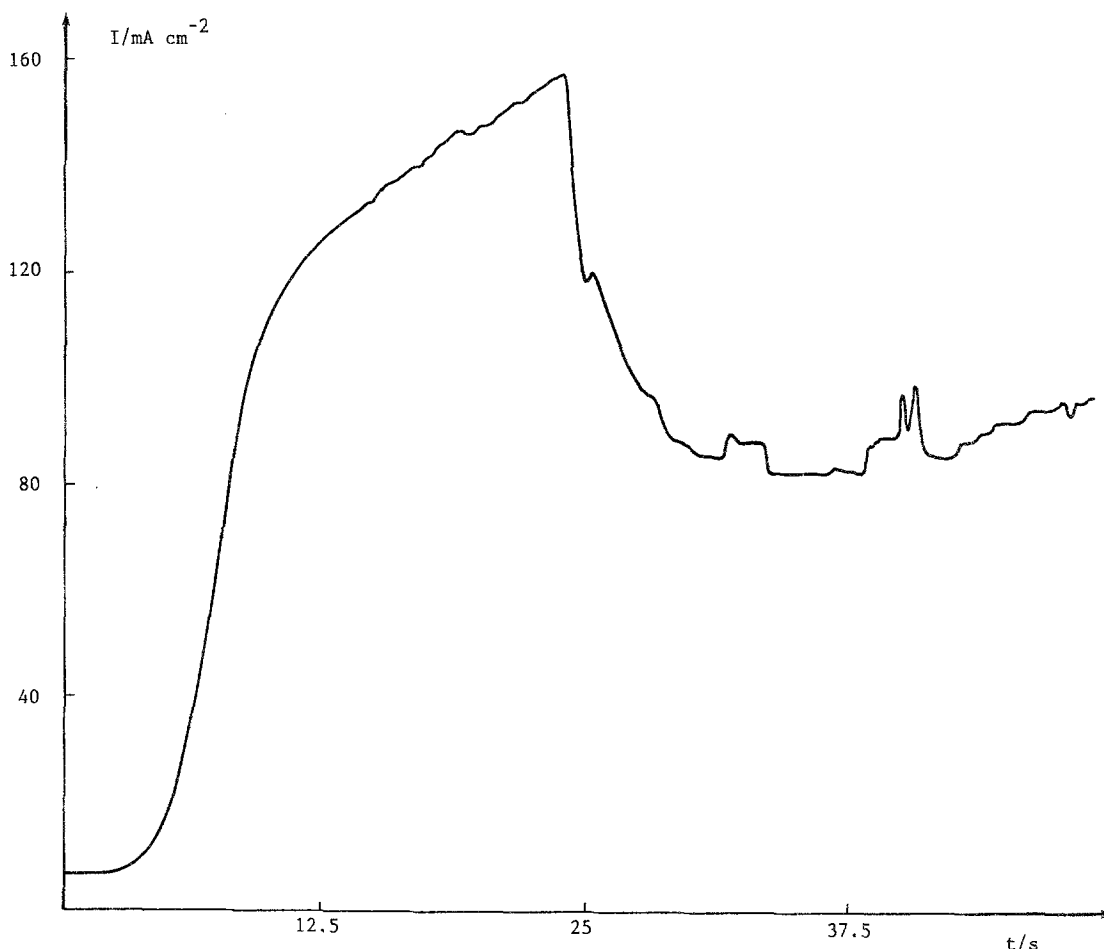


Fig. 3. $I-t$ transient over 50 s timescale for a potential step from 0 to -1.80 V. Other conditions as Fig. 2.

conducting phase is being deposited onto the carbon by a mechanism involving progressive nucleation and three-dimensional growth. On a longer timescale, rising transients could be recorded at potentials negative to -1.75 V. Further double potential step experiments were carried out; nucleation of the conducting phase was ensured by a short pulse at -1.80 V before the potential was stepped back to more positive values in the range -1.7 to -1.8 V. The observation of a rising transient at this final potential would confirm that it is the phase growth process, i.e. chromium deposition leading to at least part of the current (it should be noted that even in the experiments shown in Fig. 2, only part of the current results from the $\text{Cr(III)} \rightarrow \text{Cr}$ reaction — other reactions only occurring on the Cr serve to multiply the current at all times but do not change the shape). In fact, rising transients were observed only negative to -1.73 V showing that wave C, but not D, F or G, result from metal deposition.

Figure 3 shows the $I-t$ response to a potential step from 0.0 to -1.80 V recorded on a longer timescale than that in Fig. 2. The further features to be noted are the sudden decrease in current after about 25 s and thereafter the rather erratic response. Again, we believe that these arise from precipitation of Cr(OH)_3 onto the surface as continued H_2 evolution on the growing Cr surface causes a swing in the pH of the solution layer close to the surface (i.e. the high rate of H^+ reduction leads to the buffer capacity of the borate

solution being exceeded). Similar experiments at more negative potentials show that the change in current response occurs after the passage of a critical charge, approximately 3 C cm^{-2} .

Cyclic voltammetric experiments similar to those in Figure 1a were carried out at several temperatures in the range $0-85^\circ \text{C}$. Since the potential for nucleation is highly temperature dependent, care had to be exercised in order to select the negative potential limit so that the plateau of wave C is clearly defined, yet the precipitation of Cr(OH)_3 is avoided. This can, however, be achieved and then the $I-E$ responses are essentially similar to that of Fig. 1a. The magnitudes of the currents do vary with temperature and these are reported in Table 1. The data for the processes associated with waves C and D give linear Arrhenius plots and the energies of activation for the processes leading to waves C and D are 20 and 17 kJ mol^{-1} , respectively. These values are too large for a simple diffusion controlled reaction and suggest that either: (a) the limiting currents are diffusion limited but the equilibrium of the electroactive species varies quite strongly with temperature, or (b) the limiting currents are, at least partially, kinetically limited by the rate of a chemical reaction leading to the electroactive species. Certainly in the case of chromium deposition, wave C, the limiting currents are small compared to that expected for the diffusion-controlled reduction of the total chromium content of the solution (estimated to be

Table 1. Temperature dependence of features of the I-E curve for a C microelectrode in a solution $0.1 \text{ mol dm}^{-3} \text{ Cr}^{3+}$, borate buffer pH 3.3 and sat. K_2SO_4 . Potential scan rate 50 mV s^{-1}

Temperature (K)	Limiting current, wave C (mA cm^{-2})	Limiting current, wave D (mA cm^{-2})	Peak current, peak E (mA cm^{-2})
273	37	27	3
297	106	56	26
317	130	70	40
338	216	104	96
358	360	184	104

900 mA cm^{-2} at room temperature). Hence it is likely that there is more than one chromium(III) species in solution and that either their equilibrium concentration vary with temperature or interchange to give the electroactive species is relatively slow.

3.2. Chromium(III) in thiocyanate solutions

Figure 4 illustrates a cyclic voltammogram for a freshly resurfaced carbon fibre microdisc electrode in a solution of chromic sulphate (0.05 mol dm^{-3}), sodium thiocyanate (0.2 mol dm^{-3}), boric acid (1 mol dm^{-3}), saturated potassium sulphate and adjusted to pH 3.3. The potential scan rate was again 50 mV s^{-1} . In general, the response is very similar to that for chromic sulphate media after the addition of thiourea. The background reaction on the carbon surface, wave A,

nucleation of the metal phase at -1.80 V followed by the rapid rise in current, processes B, the chromium deposition reaction, wave C and the reductions F and G at less negative potentials can all be seen. But there is an absence of peak E. Reactions B and C are closer to the negative potential limit imposed by water reduction and there was no evidence for passivation by precipitation of a basic Cr(III) species. Potential step experiments again led to rising $I-t$ transients in the region of wave C confirming that it is, indeed, Cr deposition. At room temperature, the limiting current for this reaction is 110 mA cm^{-2} which is equivalent to 12% of the total Cr(III) content electroactive in a diffusion controlled process.

Voltammograms were also recorded for similar solutions but with thiocyanate concentrations of 0.1, 0.3 and 0.6 mol dm^{-3} . With the lowest concentration

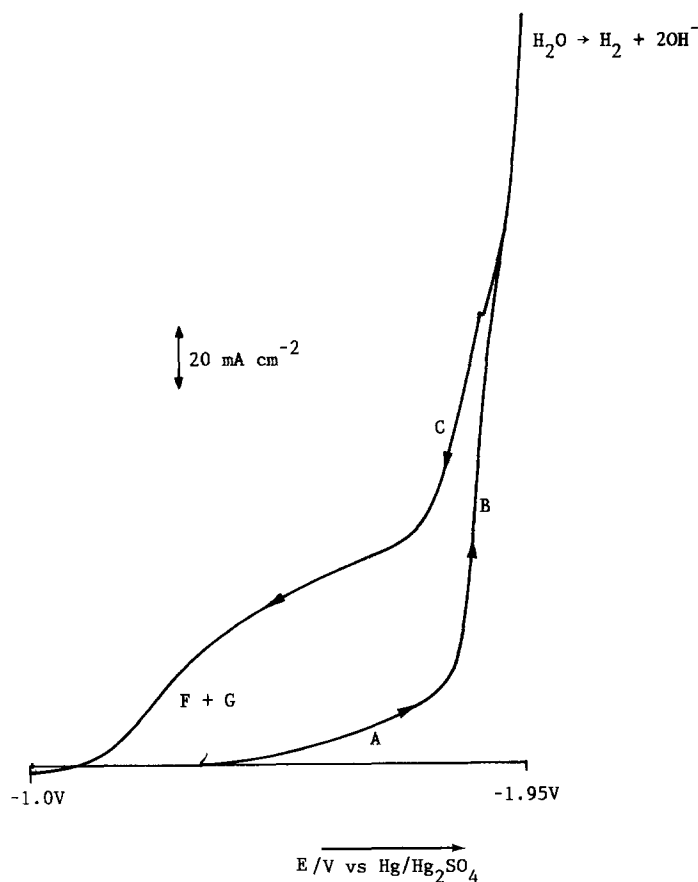


Fig. 4. Cyclic voltammogram for a freshly resurfaced carbon microdisc electrode (radius $4 \mu\text{m}$) in a solution of chromic sulphate (0.05 mol dm^{-3}), sodium thiocyanate (0.2 mol dm^{-3}), boric acid (1 mol dm^{-3}), saturated potassium sulphate and adjusted to pH 3.3. Potential scan rate 50 mV s^{-1} . Temperature 298 K.

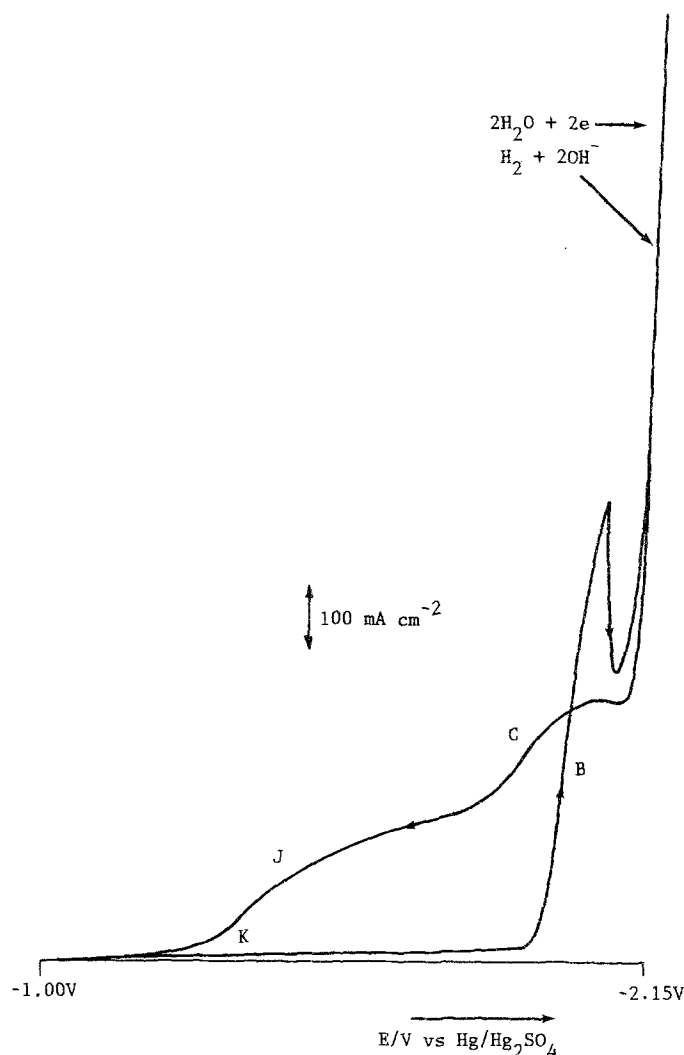


Fig. 5. Cyclic voltammogram for a resurfaced carbon microdisc electrode (radius $4 \mu\text{m}$) in the commercial chromium(III) electroplating bath, Envirochrome. Potential scan rate 50 mV s^{-1} . Temperature 298 K .

of thiocyanate, the I - E response is very similar to that in Fig. 4 except wave C is smaller with a limiting current density of 80 mA cm^{-2} . Hence less of the Cr(III) is available in the electroactive form. With both 0.3 and 0.6 mol dm^{-3} thiocyanate, neither B or C are clearly discernable and it must be concluded that with a ratio of $\text{CNS}^- : \text{Cr(III)}$ in excess of two, the potential of the Cr(III)/Cr(0) couple has been shifted to too negative a potential.

3.3. The Envirochrome plating bath

This solution was prepared according to the supplier's instructions from the components termed the liquid chromium concentrate, base salts, initial additive and wetter. Its composition is not disclosed but the chromium(III) concentration was determined to be 0.09 mol dm^{-3} by atomic absorption spectroscopy and its pH was adjusted to 3.3.

The cyclic voltammogram for a carbon microdisc electrode in this solution is shown in Fig. 5 (note this curve is recorded on a less sensitive current density scale than Figs 1 and 4). The curve shows many similarities but also some interesting differences from

those for the sulphate and thiocyanate solutions discussed above. Nucleation of the chromium metal phase is not observed until -1.91 V and thereafter the current increases rapidly until a peak is reached at -2.05 V . Whether this peak again arises because of the precipitation of Cr(OH)_3 is not clear since the response did not become erratic as in the case of the sulphate bath. Certainly the commercial bath appears to be better buffered since the current density at the peak is 850 mA cm^{-2} . The negative shift of the nucleation processes and of wave C (which is confirmed to be for Cr deposition by double pulse experiments) demonstrates that the Cr(III) is more highly complexed than in either sulphate or thiocyanate solutions. Indeed, if the potential sweep is reversed prior to the peak, process C is not observed as a well-formed wave, although the current on the reverse scan is much higher than on the forward sweep. The reverse scan also shows waves J and K; these have some similarity to waves F and G in Fig. 1 but are also shifted to more negative potentials. The anodic peak E is also absent.

Figure 6 shows I - t transients in response to potential step experiments. It can be seen that in the range -1.89 to -1.97 V , well-formed rising transients are

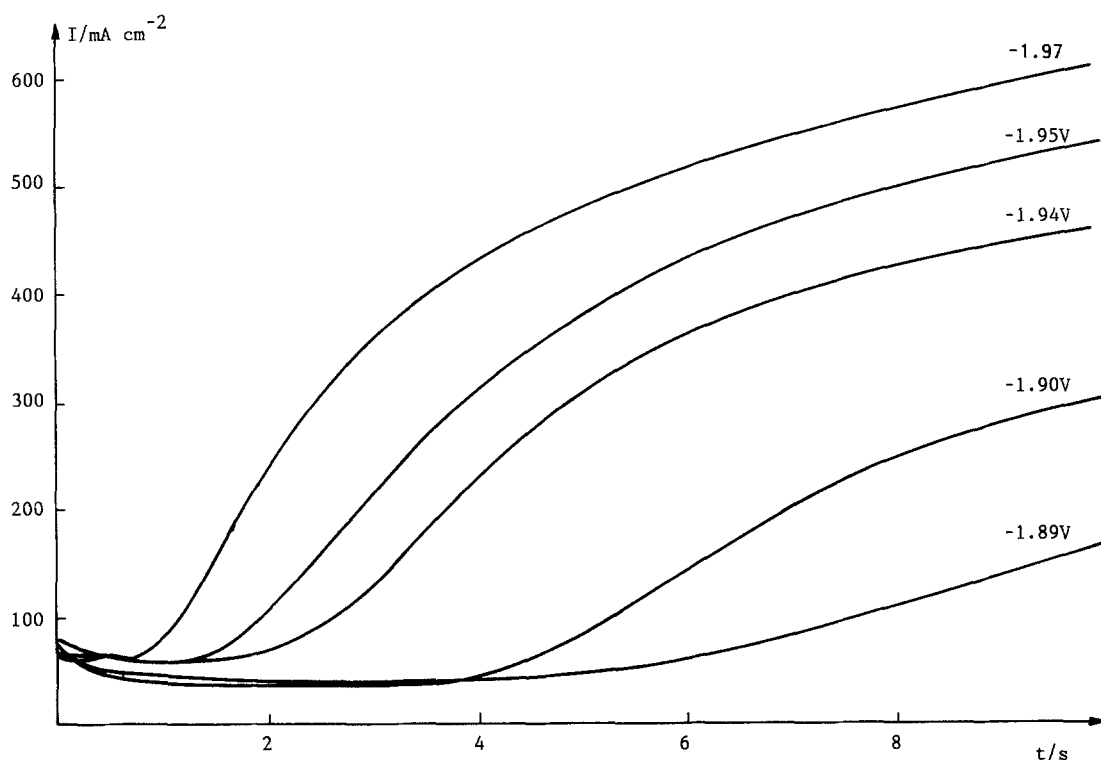


Fig. 6. I - t responses to potential steps from 0 V to the values shown. Resurfaced carbon microdisc electrode in the Envirochrome electroplating bath. Temperature 298 K.

recorded. As previously, the early part of the rising transients gives good linear $I^{1/3}$ vs t behaviour when the current for the background reduction on the carbon surface is subtracted. The plateau current increase with overpotential and can reach $> 500 \text{ mA cm}^{-2}$, although this current arises from reactions on the Cr surface ($J + K$ on the voltammogram) as well as for the metal deposition reaction. Figure 7 shows the current-time response for a pulse to -1.89 V over a much longer timescale. In contrast to the transient in Fig. 3, the plateau current is maintained over a very

long period of time. Dips such as that shown after about 30 s were frequently seen in such experiments and might result from passivation and rapid recovery. Transients such as that of Fig. 3 were only observed at potentials negative to -2.05 V .

4. Discussion

The standard potential of the Cr(III)/Cr couple in non-complexing media is reported to be -1.38 V vs a saturated mercurous sulphate reference electrode [42].

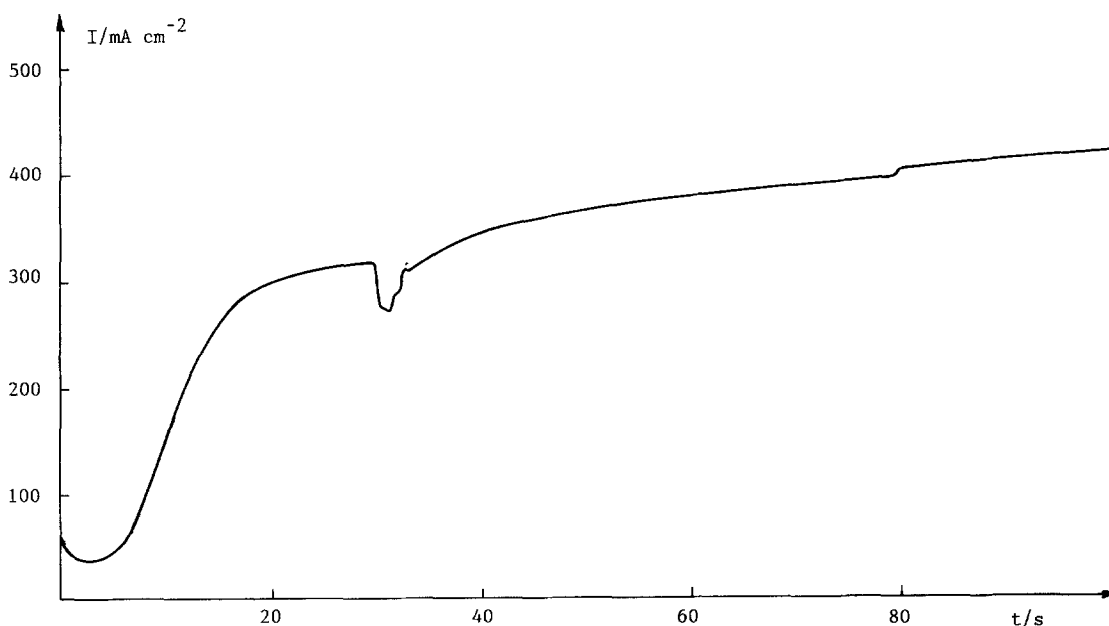


Fig. 7. I - t transient over a 100 s timescale for a potential step from 0 to -1.89 V . Other conditions as Fig. 6.

Table 2. Comparison of the characteristics for the chromium(III) plating baths

Plating bath	Nucleation potential ^a (V)	E _{1/2} for wave C ^a (V)	Max. rate Cr deposition ^b (mA cm ⁻²)	Current efficiency ^c (%)
Sulphate	-1.79	-1.73	106	63
Sulphate + thiocyanate	-1.80	-1.82	110	56
Envirochrome	-1.91	-1.95	> 250	70

^a Estimated from voltammograms at 50 mV s⁻¹.

^b Limiting current for wave C.

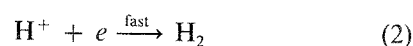
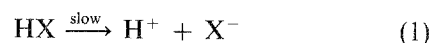
^c Ratio of limiting current wave C/total current at plateau of wave C × 100.

Of course, if the Cr(III) is present as a complex, this potential will be shifted to more negative potentials, the extent of the shift depending on the stability constant for the complex and the concentration of the ligand. The potential actually observed for the Cr(III)/Cr(0) couple, however, also depends on the kinetics of the couple in the various media. In the electrodeposition of Cr, the Cr(III) is present as a complex to suppress the hydrolysis of the metal ion and certainly to avoid the precipitation of basic compounds (e.g. Cr(OH)₃) on the Cr surface. The potential of the Cr(III)/Cr couple is probably always negative to that for the H⁺/H₂ couple (note Cr is a moderate catalyst for this couple) but it is important that H₂O reduction does not also contribute to H₂ evolution and hydroxide generation. Hence a balance must be struck between the stability of the complex to hydrolysis and shifting the Cr(III)/Cr potential too negative. Ideally the ligand should also catalyse the metal ion reduction and several sulphur ligands which adsorb on the surface of metals are known to reduce the overpotential for Cr(III) reduction [25, 31].

Table 2 reports a comparison of the data for the three Cr(III) baths studied. Both the potential for the nucleation of Cr centres and the half-wave potential for the Cr(III)/Cr reaction depend on kinetic as well as thermodynamic factors but the data would suggest that complexing of the Cr(III) decreases in the order Envirochrome > thiocyanate > sulphate. Equally, the shift to negative potentials of both the nucleation potential and wave C on addition of thiourea to the sulphate medium, see Fig. 1, is evidence that thiourea may be a ligand for Cr(III). The limiting currents for wave C are reported as an indication of the 'available' Cr(III) for reduction. Although in the absence of some passivation, no clear wave C was observed for the Envirochrome solution and hence only a minimum value can be estimated, it is clear that the current density effective for Cr deposition is much higher for the commercial solution. Hence either the equilibrium concentration of electroactive Cr(III) species or its rate of formation from inactive forms are higher in this solution than in either sulphate or thiocyanate media. It is also clear that the Envirochrome is much more efficiently buffered and it is possible to reach a current density of 850 mA cm⁻² before passivation is observed. On the other hand, it is not obvious that the current efficiency for the commercial bath is much superior to the other solutions. The ratio of the limit-

ing current of wave C to the total current at this potential is a trivial measure of this characteristic at a microelectrode, see Table 2, but it should be noted that because of differences in mass transfer to a microdisc and to an electroplate in a plating shop only the relative values are significant.

To conclude, it is necessary to summarize the origin of the various peaks and waves on the cyclic voltammograms. Process A is the commencement of H⁺ reduction on the carbon surface, a high hydrogen overpotential material. B is composite wave for Cr deposition and other processes possible on Cr but not on C surfaces. Its potential is determined by that for nucleation of Cr on the surface. Peak C is for Cr deposition alone after the nucleation and growth of a Cr layer. Peak E is probably for the corrosion and passivation of Cr metal; it is positive to the standard potential of the Cr(III)/Cr couple and compares to the potential range for active dissolution, around -1.25 V, for Cr in the more acidic solution, 0.5 mol dm⁻³ sulphuric acid [43]. The origins of peaks F and G as well as J and K are less certain. At least one of the waves in each case is due to the reduction of the weak acid [44] in the solution by reactions



which, as observed, will give rise to a kinetically controlled wave. Indeed, it may be that both waves are due to the presence of two weak acids in solution (e.g. H₃BO₃ and H₂BO₃⁻). But we have considered two other origins for one of these waves, noting that the reactions, as (2) above, must occur on Cr but not C. Firstly the reduction of thiourea or a similar additive could account for waves in some solutions; thiourea is known to adsorb on both Hg and solid surfaces [45-48] while one paper [49] reports the catalysis of thiourea reduction at an Hg cathode by several transition metal ions including Cr(III). We believe, however, that thiourea reduction is only likely at very negative potentials and in any case, we have argued above that process D is, in reality, processes F and G in the absence of thiourea (the apparent negative shift only arising because of oxidation of the Cr surface and formation of a passivating oxide layer, peak E). Secondly we considered the postulate that one of the waves is a Cr(III)/Cr(II) reduction able to occur on freshly deposited Cr but not on C. To test this hypoth-

esis, rapid cyclic voltammograms (250 V s^{-1}), feasible at microelectrodes, were recorded for the thiocyanate solution immediately following deposition of a chromium layer. An anodic peak was observed at -1.2 V but no corresponding cathodic peak, attributable to the Cr(III)/Cr(II) reduction, was seen on the sweep towards negative potentials. Hence it appears that Cr(II), if it plays any role at all, is only a transient intermediate in the Cr(III)/Cr reduction at the negative potentials.

Acknowledgement

The authors would like to thank W. Cannings Materials Ltd for the gift of the ingredients for the Envirochrome bath.

References

- [1] J. K. Dennis and T. E. Such, 'Nickel and Chromium Plating', Newnes-Butterworths, London (1972).
- [2] G. Dubpernell, 'The Electrodeposition of Chromium from Chromic Acid Solutions', Pergamon Press, Oxford (1977).
- [3] D. Pletcher, 'Industrial Electrochemistry', Chapman and Hall, London, (1982).
- [4] D. J. Barclay and W. M. Morgan, U.S. Patent 4,141,803 (1979). *Chem. Abs.* **90** (1979) 159143.
- [5] D. J. Barclay and W. M. Morgan, Fr. Patent 2,294,250 (1976) and UK Patent 1,431,693 (1976). *Chem. Abs.* **86** (1977) 179540.
- [6] D. J. Barclay and W. M. Morgan, DE. 2,723,943 (1978). *Chem. Abs.* **89** (1978) 137657.
- [7] D. J. Barclay and J. M. L. Vigar, DE. 2,943,049 (1980). *Chem. Abs.* **93** (1980) 33966.
- [8] D. J. Barclay and A. Edmund, UK Patent 1,583,105 (1981). *Chem. Abs.* **96** (1982) 43156.
- [9] D. J. Barclay and W. M. Morgan, UK. Patent 1,582,711 (1981). *Chem. Abs.* **96** (1982) 43155.
- [10] N. Deeman, European Patent 58,044 (1982). *Chem. Abs.* **97** (1982) 225668.
- [11] D. J. Barclay and J. M. L. Vigar, DE. 2,930,981 (1980). *Chem. Abs.* **93** (1980) 56949.
- [12] D. J. Barclay and J. M. L. Vigar, European Patent 35,667. *Chem. Abs.* **95** (1981) 194465.
- [13] D. J. Barclay, W. M. Morgan and J. M. L. Vigar, European Patent 79,770. *Chem. Abs.* **99** (1983) 45451.
- [14] D. J. Barclay, W. M. Morgan and J. M. L. Vigar, European Patent 79,768. *Chem. Abs.* **99** (1983) 45452.
- [15] D. J. Barclay, W. M. Morgan and J. M. L. Vigar, European Patent 79,771. *Chem. Abs.* **99** (1983) 60933.
- [16] D. J. Barclay, W. M. Morgan and J. M. L. Vigar, European Patent 79, 769. *Chem. Abs.* **99** (1983) 60932.
- [17] D. J. Barclay and W. M. Morgan, Belgium Patent 867,069 (1978). *Chem. Abs.* **90** (1979) 31148.
- [18] D. J. Barclay, N. Deeman, T. E. Such and J. M. L. Vigar, *Proc. Interfinish 80*, (1980) p. 79.
- [19] J. Gyllenspetz and S. Renton, UK Patent 1,455,841. (1976) *Chem. Abs.* **86** (1977) 179536.
- [20] T. W. Tomaszewski, H. G. Creutz and R. J. Clauss, DE 2,912,354 (1979). *Chem. Abs.* **91** (1979) 201261.
- [21] T. Berzins, US Patent 3,021,267 (1962). *Chem. Abs.* **56** (1962) 98941.
- [22] J. J. B. Ward and C. Barnes, DE 2,612,443 (1976). *Chem. Abs.* **86** (1977) 23564 and DE 2,612,444 (1976). *Chem. Abs.* **86** (1977) 23565.
- [23] I. Tsuda, N. Kasahara and M. Kobayashi, Japan Patent 77,125,427 (1977). *Chem. Abs.* **88** (1978) 81106.
- [24] J. E. Bride, US Patent 3,706,638. *Chem. Abs.* **78** (1973) 79046.
- [25] D. Smart, T. E. Such and S. J. Wake, *Trans. Inst. Met. Finishing* **61** (1983) 105.
- [26] J. C. Crowther and S. Renton, *Electroplat. Met. Finishing* **28** (1975) 6 May.
- [27] L. Gianelos, *Plating Surf. Finishing* **63** (1982) 30 March.
- [28] 'The Canning Handbook - Surface Finishing Technology', 24th edn. E & F. N. Spon, London (1986).
- [29] W. Cannings Materials Ltd, Technical Details Data Sheet 'Envirochrome Decorative Trivalent Chromium Plating Process'.
- [30] D. J. Barclay, E. Passeron and F. C. Anson, *Inorg. Chem.* **9** (1970) 1024.
- [31] M. J. Weaver, *Israel J. Chem.* **18** (1979) 35.
- [32] J. P. Hoare, Proc. 72nd Conf. Am. Electroplaters Soc. (1985).
- [33] H. Gerischer and M. Käppel, *Z. Electrochem.* **61** (1957) 463; **64** (1960) 235.
- [34] H. Gerischer and M. Käppel, *Z. Phys. Chem.* **30** (1959) 83.
- [35] J. P. Hoare, *J. Electrochem. Soc.* **126** (1979) 190.
- [36] L.-C. Jiang and D. Pletcher, *J. Applied Electrochem.* **13** (1983) 235, 245.
- [37] M. Fleischmann, S. Pons, D. R. Rolison and P. Schmidt, 'Ultramicroelectrodes', Datatech Systems, Morganton (1987).
- [38] J. D. Genders, W. M. Hedges and D. Pletcher, *J. Chem. Soc. Faraday Trans. I* **80** (1984) 3399.
- [39] W. M. Hedges and D. Pletcher, *J. Chem. Soc. Faraday Trans. I* **82** (1986) 179.
- [40] J. D. Genders and D. Pletcher, *J. Electroanal. Chem.* **199** (1986) 93.
- [41] J. N. Howarth and D. Pletcher, *J. Chem. Soc. Faraday Trans. I* **83** (1987) 2787, 2797.
- [42] A. J. Bard, R. Parsons and J. Jordan (editors) 'Standard Potentials in Aqueous Solutions', Marcel Dekker, New York (1985).
- [43] S. Haupt and H. H. Strehblow, *J. Electroanal. Chem.* **228** (1987) 365.
- [44] W. Vielstich and D. Jahn, *Z. Elektrochem.* **64** (1960) 43.
- [45] G. J. Hills and F. Silva, *J. Electroanal. Chem.* **137** (1982) 392.
- [46] M. Jurkiewicz-Herbich and J. Jastrzebska, *J. Electroanal. Chem.* **199** (1986) 201.
- [47] M. Fleischmann, I. R. Hill and G. Sundholm, *J. Electroanal. Chem.* **157** (1983) 359.
- [48] G. Horanyi and E. M. Rizmayer, *J. Electroanal. Chem.* **149** (1983) 221.
- [49] A. Baranski and Z. Galus, *J. Electroanal. Chem.* **75** (1977) 613.