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Chromium electrodeposition using a chromium(III) glycine complex

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A flow plating system was used to investigate chromium metal deposition from an electrolyte based on Cr(III) and glycine. The Cr(III) glycine species suitable for chromium deposition was identified. The chemical reactions occurring during electrolyte preparation and during metal deposition are discussed. Chemical reaction sequences for the predominant reactions are suggested. The influences of the chromium ion concentration, temperature and electrolyte velocity on chromium deposition are considered. The optimum conditions for good quality chromium metal deposition are determined.

Keywords: *chromium(III)*, *electrodeposition*, *glycine*

1. Introduction

Environmental considerations have been responsible for the increased interest in less toxic trivalent chromium electroplating solutions as an alternative to the conventional highly toxic hexavalent chromium solutions [1]. The feasibility of thick chromium plating from trivalent chromium plating baths for engineering applications has been previously investigated [2]. This initial study posed two important questions. It is still unclear what is the actual chromium(III) species that deposits chromium metal and the reason why that the plating bath ceases to deposit chromium metal in a relatively short time. This study was undertaken to investigate the chemical reactions involved in the chromium(III) plating system and to develop a better understanding of the chemistry involved during chromium deposition.

2. Experimental details

2.1. *Electrolyte*

The composition of the trivalent chromium plating baths is shown in Table 1 [2]. The chemicals were all obtained from Fisher Scientific UK.

2.2. *Electrodes*

The cathode material was copper foil of thickness 0.125 mm and purity 99.9%, obtained from Goodfellow Cambridge Ltd. High density graphite was used as the anode, obtained from Graphite Technologies PLC.

2.3. *Electroplating system*

Figure 1 shows the diagram of the electroplating system. This consisted of a plastic cell (poly vinyl chloride) with parallel cathode and anode placed 3 mm apart. The exposed area for the chromium deposition was 3 cm^2. The electrolyte solution was circulated through the cell using a Waston and Marlow 502S peristaltic pump. The power supply used was obtained from Farnell Instruments (30 V, 5 A). The temperature was maintained with the use of a Grant water bath.

2.4. *Determination of the mass of chromium metal deposited*

The mass of chromium metal removed from each bath was determined by measuring the mass of the chromium and copper substrate and then dissolving the chromium in warm HCl solution (50% volume). A sample of copper was immersed in the warm HCl solution for 1 h, no weight loss was observed. The rate of chromium deposition was measured by determining the mass of chromium deposited in a given time.

3. Results and discussion

3.1. *Chromium(III)-glycine complex*

The first objective of this study was to identify the chromium–glycine species form which chromium metal is deposited. It is known that the reaction between chromium chloride and glycine results in three main products [3], $[Cr(Gly)(H_2O)_4]^{2+}$, $[Cr(Gly)_2(H_2O)_2]^+$ and a hydrated form of $Cr(Gly)_3$, where (Gly) = $NH_2CH_2COO^-$. The glycine molecules form a chelate ring at the chromium ion bonded through their nitrogen and oxygen atoms [4]. There is evidence that the chromium complex can undergo hydrate isomerism [5]. The Cl^- ions in the outer complex enter the inner complex. An example of this is shown by

Table 1. Composition of the trivalent chromium plating baths

Component	*Concentration* /mol dm^{-3}
$CrCl_3.6H_2O$	0.3 to 1.10
Glycine	0.3 to 1.10
$B(OH)_3$	0.15
NH_4Cl	0.50
NaCl	0.50
$AlCl_3.6H_2O$	0.50

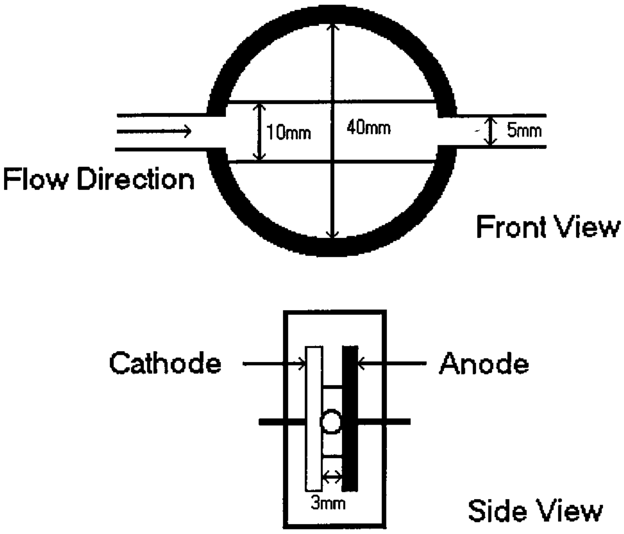


Fig. 1. Diagram of electroplating system.

$$[Cr(Gly)(H_2O)_4]^{2+}2Cl^- \rightarrow [Cr(Gly)(H_2O)_3Cl]^+Cl^- + H_2O \qquad (1)$$

3.1.1. Chromium chloride–glycine theoretical reaction model. A simple theoretical model can be devised which predicts the average number of glycine ligands bound per chromium ion for various chromium to glycine ratios. The formations of complexes in solution and the development of a simple model are dependent on three major factors [6], steric, coulombic and statistical.

Steric factor: Triphenylchromium ($Cr(C_6H_3)_3$) and other chromium arenes can be prepared relatively easily [6]. Since the glycine molecule is smaller and occupies two sites on the Cr atom, it is fair to assume that steric hindrance has little or no influence on the formation of the chromium glycine complexes.

Coulombic factor: This is a more difficult consideration. The initial reaction between chromium chloride and glycine is

$$\underset{A}{[Cr(H_2O)_6]^{3+}3Cl^- + GlyH} \rightarrow \underset{B}{[Cr(H_2O)_4(Gly)]^{2+}2Cl^-} + 2H_2O + HCl \qquad (2)$$

where (GlyH) = NH_2CH_2COOH.

When a second glycine molecule approaches both A and B, it is more likely to react with A. This is due to the negative charge on the glycine molecule after the removal of the H^+. This negative charge is attracted to the molecule with the highest positive charge, molecule A. A complication arises since the Cl^- ion can enter the inner complex as shown by Equation 1. This results in a change to Equation 2 which now becomes

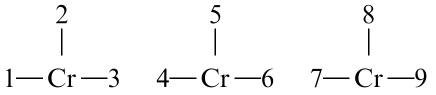
$$\underset{C}{[Cr(H_2O)_5Cl]^{2+}2Cl^- + GlyH} \rightarrow \underset{D}{[Cr(H_2O)3Gly]^{2+}2Cl^-} + 2H_2O + HCl \qquad (3)$$

In this situation both the unreacted chromium chloride and the chromium ion with a glycine ligand have the same overall charge. When a second glycine molecule approaches each molecule C or D has an equal chance of reacting.

The coulombic factors complicate the formation of a simple model, since it is believed that $[Cr(H_2O)_6]^{3+}$ is the predominant reacting species.

Statistical: Since the first two factors have limited influence, the final composition of the reaction mixture between chromium chloride and glycine is most likely based on statistical factors.

For the three chromium molecules are shown each molecule has three possible reaction sites and these sites are taken to be equivalent at any time [5].



$$1{-}\overset{\overset{2}{|}}{\mathrm{Cr}}{-}3 \quad 4{-}\overset{\overset{5}{|}}{\mathrm{Cr}}{-}6 \quad 7{-}\overset{\overset{8}{|}}{\mathrm{Cr}}{-}9$$

If these molecules are reacted with three glycine molecules, the ratio of glycine to Cr^{3+} is 1:1 (3:3). There are a number of possible outcomes in this reaction between Cr^{3+} and glycine. The three glycine molecules can occupy sites 1, 2, 3 or 4, 5, 6 or 7, 8, 9 or any of the other permutations.

A computer program was developed to calculate the total number of permutations and the total product distribution. If the glycine molecules are on positions 1, 2 and 4 then unreacted material, complex $[Cr(H_2O)_4Gly]^{2+}$ and complex $[Cr(H_2O)_2Gly_2]^+$ will all be given a value 1, $CrGly_3$ will be given the value 0. The total of these values for all the permutations of the 1:1 ratio will be taken as the product distribution for the 1:1 ratio. This was calculated by the computer program for the $GlyH/CrCl_3$ ratio 0.1 to 3.0 inclusive. Figure 2 shows the $GlyH/CrCl_3$ ratio against theoretical concentration of the unreacted material and the three glycine chromium complexes. $[Cr(Gly)(H_2O)_4]^{2+}$ is represented as complex one, $[Cr(Gly)_2(H_2O)_2]^+$ as complex two and the hydrated form of $Cr(Gly)_3$ as complex three.

This graphs represent a simple model for the products obtained in the reaction between chromium chloride and glycine.

3.1.2. Chromium chloride–glycine observed reaction model. A series of experiments was undertaken to

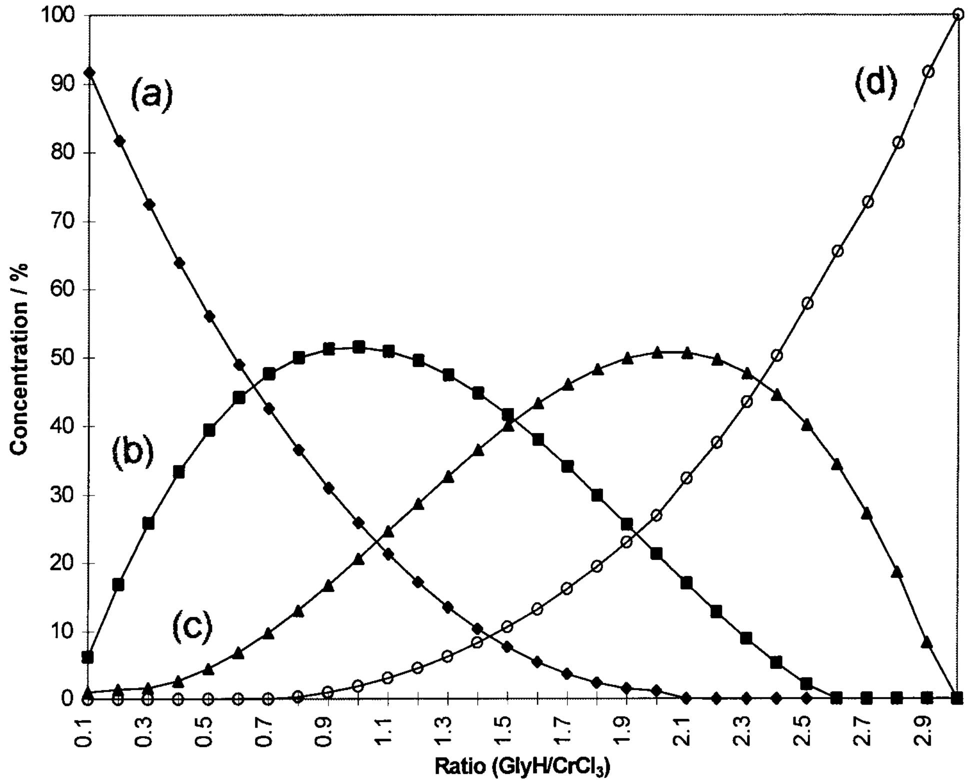


Fig. 2. Theoretical concentration of the chromium complexes against GlyH/$CrCl_3$ ratio. (a) Unreacted chromium chloride, (b) complex one, (c) complex two and (d) complex three.

establish the influence of the chromium chloride glycine ratio on the performance of the plating bath.

Fifteen plating baths each of 300 cm^3 were plated until the chromium deposition ceased. Then the total mass of chromium metal recovered determined. The conditions for each bath were: velocity 1.1 $m s^{-1}$, temperature 30 °C, chromium chloride concentration of 0.3 mol dm^{-3} and the concentration of glycine was varied between 0.06 and 1.00 mol dm^{-3}.

Figure 3 shows the plot of percentage chromium metal deposited against GlyH/$CrCl_3$ ratio. From the theoretical model it would be expected that for a GlyH/$CrCl_3$ ratio of around 1:1, 2:1 and 3:1 the most likely major products would be $[Cr(H_2O)_4(Gly)]^{2+}$, $[Cr(H_2O)_2(Gly)_2]^+$ and a hydrated form of $Cr(Gly)_3$ respectively. It is clear that the maximum chromium metal deposited corresponds to a GlyH/$CrCl_3$ ratio of around 1:1. This suggests that the only species in the electrolyte that deposits chromium metal is the $[Cr(H_2O)_4(Gly)]^{2+}$ complex. With a GlyH/$CrCl_3$ ratio of 2:1 the predominant species is $[Cr(H_2O)_2(Gly)_2]^+$, but a small amount of the complex

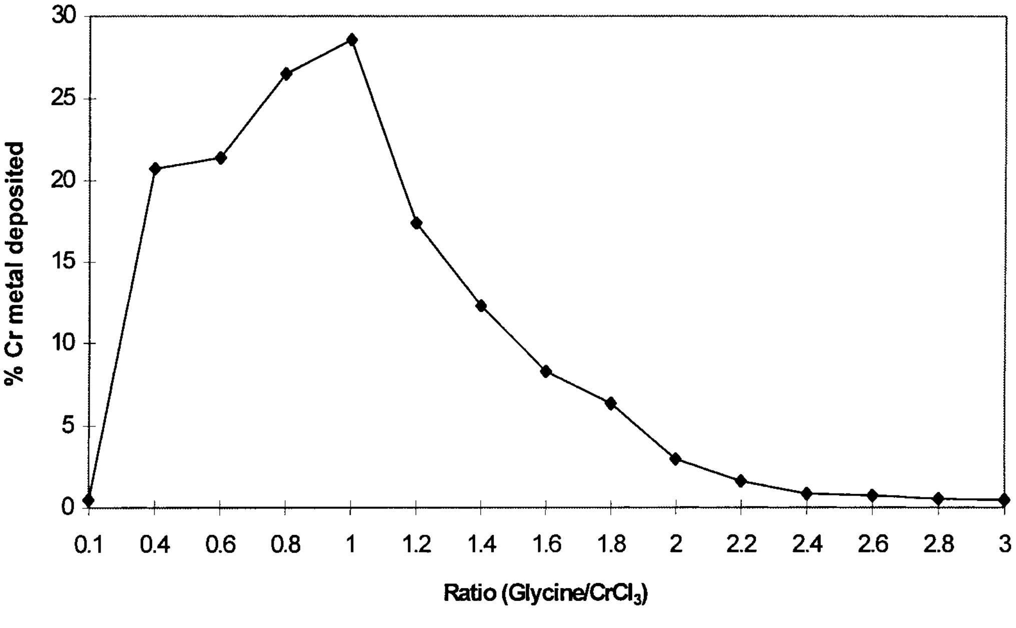


Fig. 3. Percentage chromium metal deposited against GlyH/$CrCl_3$ ratio.

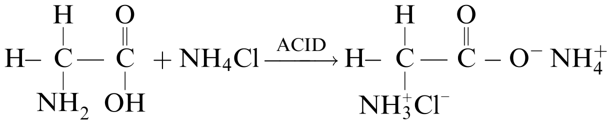
$[\mathrm{Cr(H_2O)_4(Gly)}]^{2+}$ is also present. This is the reason why at GlyH/$\mathrm{CrCl_3}$ ratios other than 1:1 chromium is still deposited.

Direct comparison between the theoretical and experimental results shows a large inconsistency between the predicted amount of chromium metal deposited and the observed. The theoretical model predicts that around 50% of chromium metal can be removed from the plating bath whereas the observed amount is around 30%, a discrepancy of around 20%. Around 10% discrepancy would be expected since it is impractical to electrodeposit all the chromium ions from the bath. The rate of chromium deposition is a function of the $[\mathrm{Cr(Gly)(H_2O)_4}]^{2+}$ ion concentration. It was determined that at a $[\mathrm{Cr(Gly)(H_2O)_4}]^{2+}$ ion concentration of 0.06 mol dm^{-2} or less the rate of chromium deposition was very low and for all practical purposes chromium deposition had ended.

3.2. *Chemical reactions during electrolyte preparation*

The main reaction during the reflux stage is between chromium chloride and glycine as shown by Equation 3. The production of HCl during the reaction reduces the pH of the solution from around 1.6 to around 0.2.

The addition of $\mathrm{NH_4Cl}$ to the electrolyte has been found to improve the consistency of the electrolyte after the initial reflux. It is probable that the $\mathrm{NH_4Cl}$ is acting as a catalyst in the reaction between chromium chloride and glycine. A suggested reaction sequence is



$$\mathrm{H{-}}\underset{\mathrm{NH_2}}{\overset{\mathrm{H}}{\mathrm{C}}}{-}\underset{\mathrm{OH}}{\overset{\mathrm{O}}{\mathrm{C}}} + \mathrm{NH_4Cl} \xrightarrow{\mathrm{ACID}} \mathrm{H{-}}\underset{\mathrm{NH_3^+Cl^-}}{\overset{\mathrm{H}}{\mathrm{C}}}{-}\overset{\mathrm{O}}{\mathrm{C}}{-}\mathrm{O^-\,NH_4^+} \qquad (4)$$

In acidic solution the glycine behaves like a base to form an amine ammonium salt [8]. The ammonium chloride can stabilise the glycine molecule to produce a more consistent reaction mixture. Chromium chloride will react with the glycine ammonium salt and form the chromium complexes, hydrochloric acid and ammonium chloride.

3.3. *Chemical reactions during chromium deposition*

Boric acid improves the quality of chromium deposits and also acts as a pH buffer at around pH 9 [9]. This gives the impression that there is a localised area of a high pH during the chromium electrodeposition. This high pH will be discussed in more detail later.

The addition of $\mathrm{AlCl_3.6H_2O}$ improves the consistency of chromium deposits over the lifetime of the electrolyte. $\mathrm{AlCl_3.6H_2O}$ form $[\mathrm{Al(H_2O)_6}]^{3+}$ hexaaquo ions in aqueous solution [5, 9] and acts as a buffer at around pH 5 [9]. With the loss of a proton the aluminium hexaaquo ion undergoes polyoxo compound formation [9]. The reaction sequence is:

$$\begin{aligned}&2([\mathrm{Al(OH_2)_6}]^{3+}3\mathrm{Cl}^-)_{(\mathrm{aq.})}\\&\quad\rightarrow [(\mathrm{H_2O})_5\mathrm{Al{-}OH{-}Al(OH_2)_5}]^{5+}5\mathrm{Cl}^-\\&\quad + \mathrm{H_2O} + \mathrm{HCl} \qquad (5)\end{aligned}$$

The influence of $\mathrm{AlCl_3.6H_2O}$ on the electrodeposition process is not completely understood at this stage.

3.3.1. Anode reaction. The predominant reaction at the anode is the production of chlorine gas.

$$2\mathrm{Cl}^- \rightarrow \mathrm{Cl_2} + 2\mathrm{e}^- \qquad (6)$$

No Cr^{6+} as dichromate has been detected in the electrolyte solution after operation. This is a good indication that the oxidation of Cr^{3+} to Cr^{6+} at the anode is not a significant problem.

3.3.2. Cathode reactions. The production of hydrogen gas and chromium metal take place. The suggested reaction sequences are shown by Equations 7, 8 and 9, respectively.

$$\mathrm{Cr}^{3+} + 3\mathrm{e}^- \rightarrow \mathrm{Cr}_{(\mathrm{metal})} \qquad (7)$$

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H_2} \qquad (8)$$

$$\begin{aligned}&2([\mathrm{Cr(H_2O)_4(Gly)}]^{2+}2\mathrm{Cl}^-) + 2\,\mathrm{NH_4Cl}\\&\quad\rightarrow 2\,\mathrm{Cr}_{(\mathrm{metal})} + 2\,\mathrm{GlyNH_4} + 3\,\mathrm{Cl}_{2(\mathrm{gas})} + 8\,\mathrm{H_2O} \qquad (9)\end{aligned}$$

The reaction sequence suggested by Equation 9 is based on the Gly^- ion being stabilized by the ammonium ion to form an ammonium salt with the evolution of chlorine gas. The ammonium chloride in Equation 9 could be replaced by NaCl, the products being a sodium salt and chlorine gas. HCl could also replace $\mathrm{NH_4Cl}$ or NaCl in Equation 9. The products in this case would be glycine and chlorine gas. It is likely that $\mathrm{NH_4Cl}$, NaCl or HCl reacts with the glycine anion.

3.4. *Chromium deposition*

A series of experiments were carried out to investigate the rate of chromium deposition and to establish the influence of both the $\mathrm{CrCl_3}$ concentration and the velocity of the electrolyte on the chromium deposition.

3.4.1. Chromium chloride concentration. Six 300 cm^3 plating baths were prepared with $\mathrm{CrCl_3}$ concentrations of between 0.1 and 1.1 mol dm^{-3}. The $\mathrm{CrCl_3}$–GlyH concentration was maintained at the ratio of 1:1. These six baths were operated until the deposition of chromium metal ceased. The average current density was around 95 A dm^{-2}. Chromium metal was deposited for 30 min on a number of copper substrate samples. The mass of chromium metal removed from each bath was determined. The concentration of $\mathrm{CrCl_3}$, the percentage mass of chromium metal removed from each bath and the rates of deposition are shown in Table 2.

3.4.2. Electrolyte velocity. The electrolyte flow was achieved with a peristaltic pump. The pump is pulsed

Table 2. Mass and rate of chromium deposition for various $CrCl_3$ concentrations at 50 °C

Conc. $CrCl_3$ /mol dm^{-3}	*Mass of Cr metal deposited* /%	*Rate of Cr metal deposited* /10^{-3} g min^{-1}
0.1	0.13	0.7
0.3	28.97	3.0
0.5	29.48	3.8
0.7	18.68	2.4
0.9	17.73	2.0
1.1	17.62	1.6

in nature and this flow characteristic will slightly agitate the electrolyte solution as it flows through the cell. This has not been found to be a significant problem. A continuous none pulsed flow would be more desirable but the corrosive nature of the electrolyte, the relatively small volumes used and the ease with which the flow rate can be varied makes the peristaltic pump the preferred option. Six 300 cm^3 plating baths were prepared with $CrCl_3$ and glycine concentrations of 0.3 mol dm^{-3}. The temperature was maintained at 50 °C. These baths were operated until the deposition of chromium metal ceased. Six different electrolyte velocities were used with a current density of 95 A dm^{-2}. The mass of chromium metal deposited was determined. Since the total mass of chromium within the bath is known, the percentage mass of chromium removed from the baths was calculated. The results are shown in Table 3.

3.4.3. Rate of chromium deposition. A plating bath was prepared with a $CrCl_3$ and glycine concentration of 0.3 mol dm^{-3} and volume of 1800 cm^{-3}. This bath was divided into six equal volumes each of 300 cm^3. The temperature was maintained at 30 °C, current density at 40 A dm^{-2} and an electrolyte velocity of 1.11 m s^{-1}. The rate of deposition is influenced by both the temperature of the electrolyte and the concentration of the plating ion. With this low rate of deposition only a small amount of chromium metal is removed from each bath. With these conditions the plating ion concentration is expected to have no significant influence on the rate of deposition.

The first 300 cm^3 of the solution was operated for 10 min the second for 20 min and so on to 60 min. The masses of the chromium metal deposits were determined and plotted against time. The rate of deposition was determined from the slope of this graph. The resultant straight line indicated that the rate of deposition was independent of the plating ion concentration.

This was repeated at 35, 40, 45 and 50 °C. The rates of chromium deposition at these temperatures are shown in Table 4. The rate of chromium deposition decreases with increased temperature.

3.4.4. Discussion of experimental observations. There are three observations from these experiments:

(i) The theoretical model is not consistent with the observed model.
(ii) The optimum $CrCl_3$ concentration is 0.5 mol dm^{-3}.
(iii) The optimum velocity for this plating system is 0.96 m s^{-1}.

An explanation for these can be based on the production of NaOH due to the electrolysis of NaCl and NH_4Cl. These reactions are

$$2\,NaCl + 2\,H_2O \rightarrow H_{2(gas)} + Cl_{2(gas)} + 2\,NaOH \tag{10}$$

$$2\,NH_4Cl + 2\,H_2O \rightarrow H_{2(gas)} + Cl_{2(gas)} + 2\,NH_4OH \tag{11}$$

The reaction at the cathode is shown by

$$2\,Na^+ + 2\,H_2O + 2\,e^- \rightarrow H_{2(gas)} + 2\,NaOH \tag{12}$$

The discrepancy between the predicted mass of chromium removed from the bath and the observed is possibly due to the plating ion being rendered inert due to its reaction with OH^- ions. The proposed reaction is:

$$[Cr(Gly)(H_2O)_4]^{2+} + OH^- \rightarrow [Cr(Gly)(H_2O)_3(OH)]^+ + H_2O \tag{13}$$

The resulting complex will not deposit chromium metal during electrodeposition.

The optimum chromium chloride concentration for the maximum mass of chromium metal deposited is around 0.5 mol dm^{-3} at electrolyte velocity of 0.96 m s^{-1}.

A possible explanation for these observations is again based on the deactivation of the chromium complex by OH^- ions. The rate of chromium deposition is controlled by the rate of migration chromium

Table 3. Mass of chromium metal deposited at various electrolyte velocities at 50 °C

Velocity /m s^{-1}	*Mass of Cr deposited* /g	*Mass of Cr deposited* /%
0.09	0.227	4.85
0.17	0.254	5.42
0.43	0.278	5.93
0.72	1.370	29.27
0.96	1.380	29.48
1.11	1.356	28.97

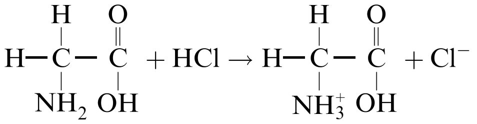
Table 4. Rate of chromium metal deposition for various temperatures at 40 A dm^{-2} and electrolyte velocity of 1.11 m s^{-1}

Temperature / °C	*Rate of deposition* / 10^{-3} g min^{-1}
30	2.28
35	1.96
40	1.83
45	1.73
50	1.67

ion through the diffusion layer [10]. The initial increase in chromium ions concentration increases the deposition rate until it reaches the rate of the migration process. The initial rate is dependant on chromium ion concentration then becomes dependant on the rate of migration. Similarly the initial increase in the electrolyte velocity increases the deposition rate until it reaches the rate of the migration process. The initial rate is dependant on the electrolyte velocity then becomes dependant on the rate of migration. It would be expected that at the higher chromium ion concentrations or higher electrolyte velocities the rate would remain constant. A possible reason for the rate decrease is the fact that chromium plating ions reside for a longer time in the vicinity of the diffusion layer and their probability of undergoing reaction with OH^- ions is greatly enhanced.

3.5. *Beneficial effect of hydroxide ions at the cathode*

The initial impression is that if the OH^- ions at the cathode are reduced or completely removed, the performance of the plating system will be improved. It was suggested by Equation 9 that after the chromium metal is deposited, the glycine anion will be stabilised by an ammonium ion. This reaction will be predominant in an alkaline environment. It is possible that the OH^- ions are beneficial in the chromium deposition process. It is shown by Equation 4 that the glycine in an acid solution behaves like a base to form an amine salt [8].



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle NH_2}{C}}{-}\overset{\displaystyle O}{\underset{\displaystyle OH}{C}} + HCl \rightarrow H{-}\overset{\displaystyle H}{\underset{\displaystyle NH_3^+}{C}}{-}\overset{\displaystyle O}{\underset{\displaystyle OH}{C}} + Cl^-} \qquad (14)$$

If the environment in the diffusion layer was acidic, the glycine anion would be deposited on the cathode during the deposition of chromium metal. Not only glycine shed from the chromium complex would be deposited but also the unreacted glycine contained in the electrolyte. When the pH of the electrolyte is lowered by the addition of dilute HCl there is a distinctive reduction in the quality of the chromium metal deposits. This is consistent with the formation of the glycine anion and by the reaction sequence shown in Equation 14. It is probable that this anion is being deposited on the cathode and contaminating the chromium metal deposit. The deposition of glycine on the cathode is a known source of chromium metal contamination [11].

4. Conclusion

There is evidence to suggest that the $[Cr(Gly)(H_2O)_4]^{2+}$ ion is the species that deposits chromium metal. Since the reaction between chromium chloride and glycine results in a number of products it will be necessary to develop a method to produce this ion in a pure form. This considerably reduces the cost of chromium deposition enhances the commercial feasibility of the process. When the quality of chromium deposits and the amount of chromium removed from the bath are taken into consideration, the optimum conditions for the plating system are a chromium chloride concentration of $0.5\,\mathrm{mol\,dm^{-3}}$, a flow rate of $0.96\,\mathrm{m\,s^{-1}}$, a current density $90\,\mathrm{A\,dm^{-2}}$ and a temperature of 40 °C.

Acknowledgements

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