



Full Length Research Article

A NOVEL STUDY ON CHROMIUM ELECTROCHEMICAL DEPOSITION FROM CR(III)-GLYCINE COMPLEX SOLUTION

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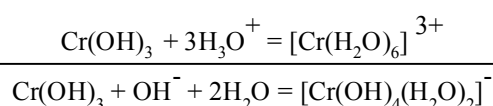
ABSTRACT

The chromium plating solution was prepared from Cr (III) salt mixed with a suitable chelating organic agents. The ratio of chelating agent concentration with Cr (III) concentration was selected object of this study before to apply in practice. Amino-acetic acid chelating compound was agent capable to form the complex with the Cr (III) ions but depending on the ratio of these substances present in solution. In this paper, the research was focused on the complexing of amino-acetic acid and Cr(III) ions, evaluation of plating capabilities of the complexes based on determining the reaction rate during scanning, CV. The experiment shows that the complex of Cr(III)-glycine exhibited an excellent compound to use in chromium electrochemical deposition. By this way the optimal Cr (III) and chelating agent concentration were selected for making decorative chromium plating solution.

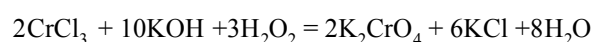
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INTRODUCTION

Electrochemical plating from Cr (III) solutions depends strongly on the nature of Cr (III) complex with different ligands (Tran Minh Hoang, 2000, K. Dennis, T.E. Such, 1993, N.V. Mandich, D.L. Snyder, 2000), One of the chelating agents that are interested is the amino- acetic acid, an amino acid called glycine acid (Elisabete S.C. et al., 2013). The compound Cr (III) is generally toxic salts but lower Cr(VI). There are many Cr(III) salts having the properties and composition like the Al(III) salt, due to their ion size are similar such as Cr(III) (0.57 Å) and Al(III) (0.61 Å). Likewise Cr (OH)₃ exhibits properties similar to Al (OH)₃; they can form colloidal, chartreuse, insoluble in water and being amphoteric. The fresh Cr (III) hydroxide dissolved easily in acid, base as following reactions:



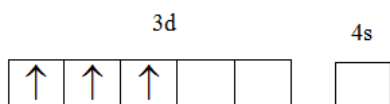
The formed ions like $[\text{Cr(OH)}_4(\text{H}_2\text{O})_2]^-$, $[\text{Cr(H}_2\text{O)}_6]^{3+}$ are less stable, when heated, easily decompose in solution to form Cr(OH)₃ precipitated. The fresh Cr(III) solution exhibits a red purple at room temperature, but then turned into green when heated (red purple is the characteristic color of the ion $[\text{Cr(H}_2\text{O)}_6]^{3+}$). Cr(III) salt is paramagnetic compound, very durable in dry air and stronger hydrolysis than Cr(II) salt. In an acid environment, Cr(III) ions are reduced to Cr(II) by metallic zinc. But in alkaline Cr(III) can be oxidized by H₂O₂, PbO₂, chlorine water, bromine water to form chromate as follows:



Due to the big radius and charge of the Cr (III) ion it is one of the strong chelating agents that can form complex with the most known ligands. However, the stability of the Cr(III) complex still depends on the nature of the ligand and complex configurations. Electron configuration of Cr atoms is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹, when losing 3e formed Cr(III) with single electron three, two empty orbitals in 3d- subclass, and with one empty orbital in subclass 4s so that the ability to form Cr(III) complex like anion and cation complexes becomes more easily. The electron configuration of Cr(III) is as follows

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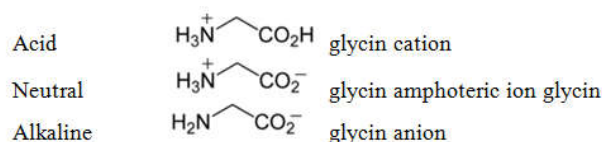
Since being the intermediate state, Cr(III) ions exhibits both oxidizing (in acidic) reducing (in the environment or base) characteristics. Many Cr(III) complexes with coordination number of two, three, four in which ligand might be neutral molecules as

H_2O , NH_3 , $-\text{NH}_2^-$, $-\text{CH}_2-\text{CH}_2-\text{NH}_2$ or acidic as Cl^- , $(\text{SO}_4)^{2-}$, $(\text{C}_2\text{O}_4)^{2-}$, $(\text{SeO}_4)^{2-}$, HCOO^- .

Aminoacetic acid chelating agents (symbol AAA)

Aminoacetic acid with chemical formula $\text{NH}_2\text{CH}_2\text{COOH}$, usually denoted by AAA is an amino acid (acid glycine) and also an enzyme.

AAA in the aquatic environment can transform into the anionic or cationic ions depending on the pH of the solution as the following diagram:



Three types of these ions can be transformed into each other depending on pH values. Glycine has the formula shown in Figure 1a or 1b as follows

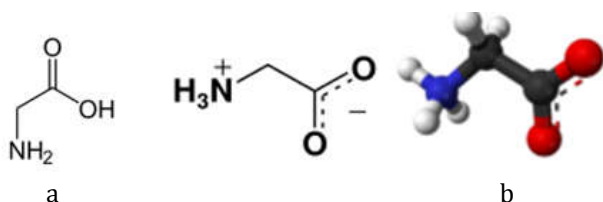


Figure 1. Some configurations of AAA

The AAA Cr(III) complex is a complex of amino acids (Elisabete S.C. *et al*, 2013, Kun Sri Budiasih, *et al*, 2013, Toepfer, E.W.*et al*, 1977). A good method of preparation of amino acid Cr(III) complexes has been illustrated by their stability, repeatability, and especially electrochemical activation (Bryan, RF.*et al*, 1971, Wallace, W.M., *et al*, 1982). The synthesis of complexes between Cr(III) - glycine with a high repeatability is very hard if does not maintain stable synthetic conditions (Guindy NM., *et al*, 2000, Kita, E., *et al*, El Sahrawi, 1995). Previously there have been studies on this complex synthetic process (Bryan RF, 1971). Recently the preparation of the complex Cr(III) - AAA with improvements has been completed. The complex was prepared by mixing the $(\text{CrCl}_3 \cdot 6\text{H}_2\text{O})$ -liquid reflux, glycine and sodium hydroxide according to the molar ratio of 1:3:3 for 3 hours (Kun Sri Budiasih *et al*, 2013). In aqueous solution containing ions Cr(III), depending on the molar ratio between Cr(III) and glycine the complexes can create the following forms (J. Mc DOUGALL, *et al* 1998, Anil Baral *et al* 2005, A. M. Smith, *et al* 1993):

Monoglycine: $\text{Cr}[(\text{H}_2\text{N}-\text{CH}_2-\text{COO})(\text{H}_2\text{O})_4]^{2+}$
 Diglycine: $\text{Cr}[(\text{H}_2\text{N}-\text{CH}_2-\text{COO})_2(\text{H}_2\text{O})_2]^+$
 Triglycine: $\text{Cr}[(\text{H}_2\text{N}-\text{CH}_2-\text{COO})_3]$

Thus the molar concentration ratio of Cr(III) and AAA can affect the formation, structure, and components of complexes. Without existing complex, only ion Cr(III) or AAA individual chelating agents in solution studies (ammonium sulfate, boric acid) do not appear the reduction reaction kinetics. This paper has introduced the kinetic research results of of Cr(III)-AAA complex deposition in solution with boric acid and ammonium sulfate.

Experimental part

Preparation of Cr(III)- AAA complex

Chemicals: All chemicals such as CrCl_3 glycine, ammonium sulfate, boric acid were bought from Merch Company. Take initial concentration of AAA 0.8m and Cr(III) concentrations, the ratio $\tau_{\text{Cr}} = [\text{Cr(III)}]/[\text{AAA}]$, $\tau_{\text{A}} = [\text{AAA}]/[\text{Cr(III)}]$ listed in Table 1.

Table 1. Cr(III) conc. and $\tau_{\text{Cr}}, \tau_{\text{A}}$

$C_{\text{Cr}^{3+}}, \text{M}$	0.05	0.10	0.20	0.30	0.50	0.80
C_{A}, M	0.80	0.80	0.80	0.80	0.80	0.80
τ_{Cr}	0.063	0.125	0.250	0.375	0.625	1.00
τ_{A}	16.00	8.00	4.00	2.67	1.60	1.00
Symbol	Dd 1	Dd 2	Dd 3	Dd 4	Dd 5	Dd 6

Experimental method

Cyclic voltammetry method (CV) was implemented by the instruments suggested in the document (Allen J. Bard, *et al* 2001). In the CV method the potential was linearly increasing to a certain value then decreasing linearly on the initial value (Figure 2). Meanwhile polarization potential dependence E_t was given by the equation

$$E = E_{\text{sta}} + v(t-2\lambda)$$

in which: - E_{sta} is initial potential, mV

- v : scanning rate, mV/s

- λ the reaction time corresponding to half the scanning cycle, s

When $t = \lambda$ polarization voltage reaches the value "end" E_{end} , point b in Figure 1, then descending to E_{sta} . The C2 cycle polarization process was repeated in circulation. The polarized multi-cycle method (CV) is a strong electrochemical method that allows to survey kinetics and also mechanism of electrode reactions (Toepfer *et al.*, 1977).

RESULTS AND DISCUSSION

Formation of complex

The formation of the Cr(III)-AAA was characterized by the appeared color of solutions. The obtained complex solution with different colors depends on the composition ratio $\tau_{\text{A}} = C_{\text{AAA}}/C_{\text{Cr(III)}}$, $C_{\text{AAA}} : 0,80\text{M}$ and Cr(III) varying from 0.05M to 0.80M.

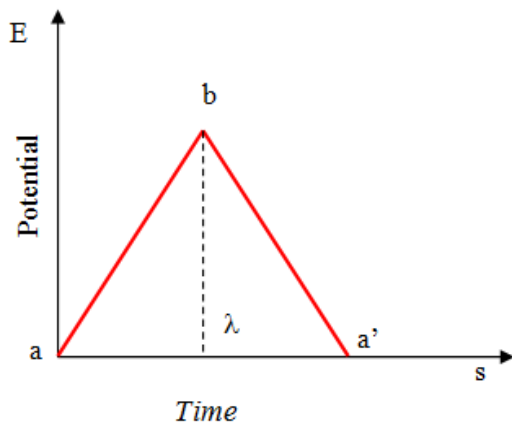


Figure 2. Voltage variations vs. time in the multi cycle-scanning method

As the Cr(III) concentration decreasing the complexes were formed such as monoglycin forms, diglycine and triglycin respectively in solution. If τ_{Cr} is small so that the complex of Cr(III)-triglycine will dominate. When τ_{Cr} increases the complexes of Cr(III) with diglycine and monoglycine will dominate in solution. After dispensing the plating solution according to the ratio as Table 1, the obtained plating solutions were denoted as numbers 1, 2, 3, 4, 5, 6 respectively with different colors as follows

- Solution 1: purple red
- Solution 2: black purple
- Solution 3, 4: black green, black solution of 3 was darker than 4 solution.
- Solution 5, 6: green, the green color of 6 was stronger than 5- solution

Influence of $\tau_{Cr} = [Cr^{3+}] / [AAA]$, τ_{Cr} varying from 0 to 1 Study on CV cathode rate method

The solutions after the preparation were contained in glass bottles for a day before measuring CV.

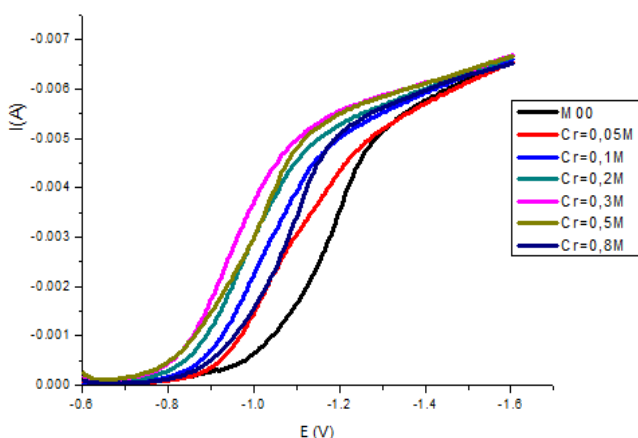


Figure 3. Cathode branch of the CV curve with the different τ_A or τ_{Cr} ratio

The solutions were scanned (CV) using copper cathode electrode with an area of 0.20 cm² and composite TiO₂ / RuO₂ coated titanium mesh anode. A blank sample solution, M00 consists of ammonium sulfate, boric acid, their concentration and their pH like in the plating solutions 1-6. CV cuves obtained are presented in Figure 3. Compared with the cathode branch curve of the blank (M00), slope of the cathode branch

curve of the solutions 1 to 6 have changed, and the cuves position was shipted to more positive potentials. When the concentration of the complex Cr(III) are gradually increasing the cathodic CV currents also increase. This variation means there was a formation of different Cr coating as the result of cathodic reduction of Cr(III) complex in solution.

The dependence of electric current density J on the ratio τ_{Cr} , between the voltages from - 0.60 to -1.00V

Figure 4 shows that, when the polarization potential was small, there was an insignificant change in I current, but when the potential polarity increased from -0.60V to -1.00V cathodic reaction line in solutions also rose more sharply. The I current also depends on τ_{Cr} . There was a maximum I current at $\tau_{Cr} = 0.375$, then decreased in the rate of τ_{Cr} increasing.

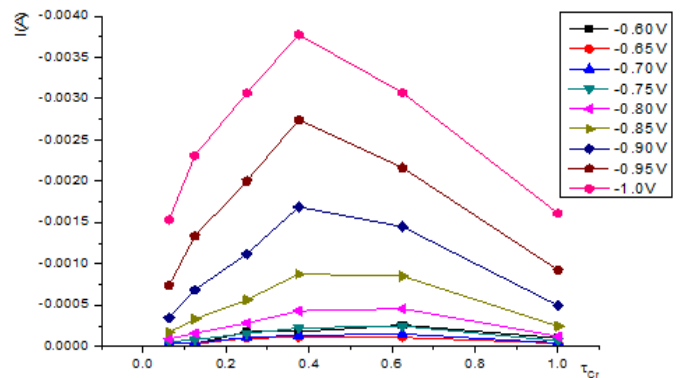


Figure. 4 The change of the electric current density J according to τ_{Cr} at different voltages

The dependence of I on τ_{Cr} in the voltages from -1.00 to 1.40 V

Figure 5 shows, the polarization potential increased from -1.00V to -1.40V cathodic current has risen, reached maximum at $\tau_{Cr} = 0.375$. However, at the polarization potential more -1,25V current (I) in different solutions were negligibly increasing, tended to equal.

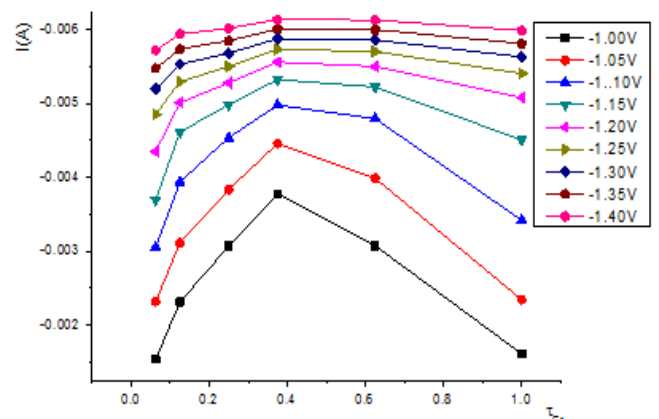


Fig. 5. The dependence of Ion τ_{Cr} in the voltage from -1.00 to -1.40V

Influence of I on τ_{Cr} in the voltages from -1.40 -1.65 V

The Fig. 6 shows, when the voltage continues increasing, the change of the current density I versus τ_{Cr} was not significantly different. With ratio τ_{Cr} increasing the I lines increase and then decrease.

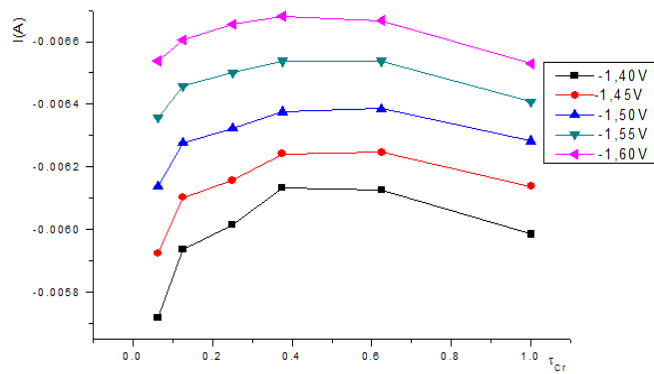


Figure 6. The dependence of Ion the τ_{Cr} in the voltage from -1.40 to -1.65 V

Study of Cr(III)-complex reaction at cathode

Net discharge curve of the complex Cr(III) on the cathode

Figure 7 shows a variation of net discharge current I on Cr(III) complex at the cathode in the solution including Cr(III) varying from 0.05M to 0.80M and concentration of AAA-complexing agent 0.80M. In the plating process, according theory, beside the metal precipitated the hydrogen also exhausted. When curves of the cathode plating branch was measured in solution from sample 1 to 6 minus cathode curve branch of sample M00 we obtain net curve of Cr(III) complex reaction. The curves show that in the plating solution discharge speed of net complexes is disparate

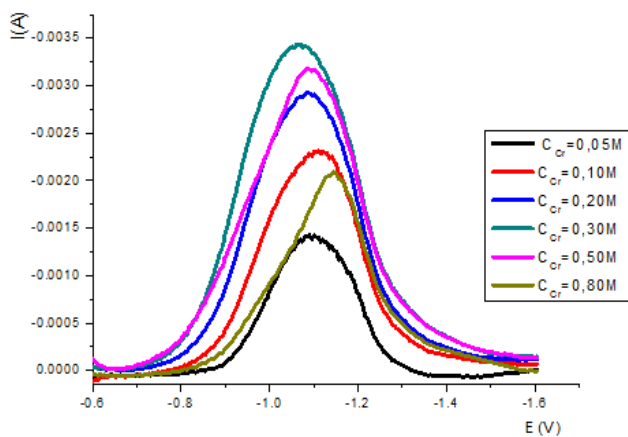


Fig. 7. Net discharge flows of Cr(III) complexes at cathode electrode

The dependence of Net Cr(III) complex on ratio τ_{Cr}

The voltage range form - 0.60 to -1.00 V

Figure 8 shows the variation of current velocity for the potential range from -0.60V to -1.00V corresponding to τ_{Cr} . At the low potential cathodic reduction rates changed little and insignificantly. When the polarization potential reaches up to range -0.80V to -1.00 V, the reaction rate increases to maximum value at $\tau_{Cr} = 0,375$. At this ratio the form Cr(III)-diglycine complex might be formed mainly. This complex might exhibit small over potential so that is favorite to precipitate chromium at electrode. When τ_{Cr} ratio rises the monoglycine complexes can be formed mainly containing water molecules with great over potential so hardly reducing at electrode causing smaller reaction current.

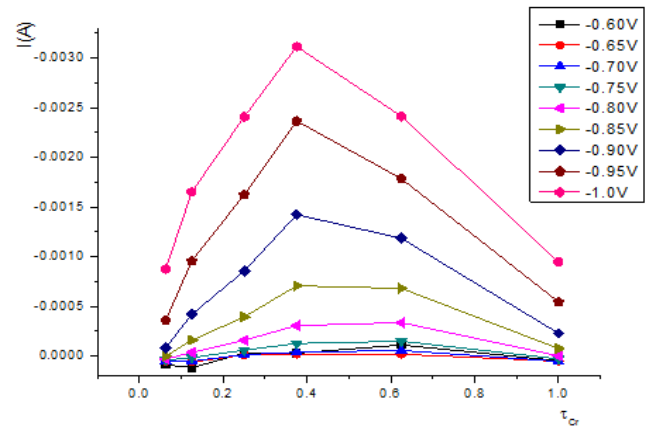


Figure 8. The dependence of the net reaction current of Cr(III) complexes on τ_{Cr} in the voltage range from - 0.60 to -1.00 V

The dependence of the net reaction current of Cr(III) complexes on τ_{Cr} in potential range -1.00V to -1.40 V

Fig. 9 shows the changes in net flows of complexes Cr (III) in the range of voltages from -1.00 to -1.40V according τ_{Cr} . When the voltage gradually increased the net flows continue to increase with the t_{Cr} increasing and reached a maximum at the voltage of -1.05V.

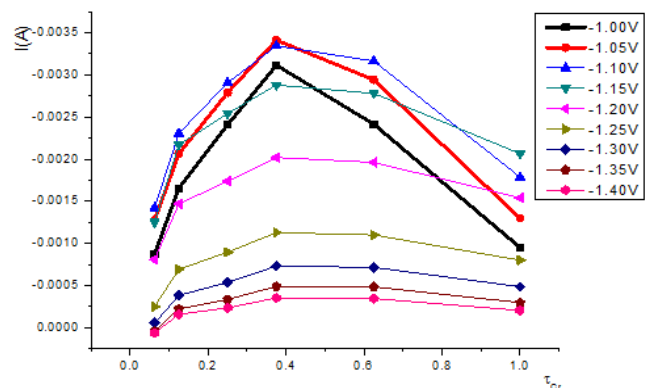


Figure 9. The dependence of the net reaction current of Cr(III) complexes on τ_{Cr} in potential range -1.00V to -1.40 V

At the same potential value, the peak of the net currents appear at $\tau_{Cr} = 0.375$. When the CV potential increases from -1.20V to -1.40V the net current lines of complexes at the ratio of τ_{Cr} differ slightly. It means that the net currents of monoglycine complex increased almost at par with complex or diglycine or triglycine. At each different ratio of τ_{Cr} there were various kinds of complex formed in the solutions. At the Cr(III) concentrations were very small corresponding $\tau_{Cr} = 0.063$; 0.125, in solution the complex with triglycine would be formed but with low concentrations and caused the small discharge speed and small precipitation of chromium at electrode. When Cr(III) concentration increased ($\tau_{Cr} = 0,25$), the Cr(III) complex of triglycine, would be highly formed leading net current rate increasing. When Cr(III) concentration continues to rise ($\tau_{Cr} = 0,375$; 0,625) in solution the diglycine complex might be formed, with the its high electrical discharge causing the high net current. This net current reaches to the maximum value at $\tau_{Cr} = 0.375$ and then decreases due to forming Cr(III) complex with monoglycine. Overall, the complex kinds of triglycine and monoglycine exhibit that at the cathodic electrode their electrical discharge rate is smaller than Cr(III) diglycine complex.

The dependence of the net reaction flow of Cr(III) complexes on τ_{Cr} in potential range from -1.40V to -1.60V

At the voltage in the range from -1.40 to -1.60V, the net reaction flow of Cr(III) complexes versus to the ratio of τ_{Cr} decreases. It is possibly that in more negative voltage values, beside the Cr (III) complex discharged there is also discharge of impurities or other

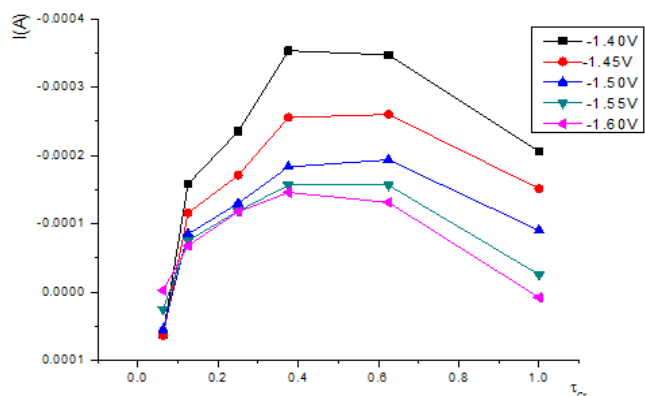


Figure 10. The net reaction current of Cr(III) complexes variation as a function of τ_{Cr} , potential range -1.40V to -1.60V

Conclusions

The electrochemical plating using Cr(III) with amino acetic acid (called glycine - AAA) was studied in detail using CV polarization in this paper, as a novel investigation technique for Cr(III) plating kinetics. The plating solution using glycine chelating agents with the concentration of 0.80M, Cr(III) concentrations varying from 0.25M to 0.50M, corresponding to the ratio of $\tau_{Cr} = 0.250; 0.375; 0.625$, can be used for the chromium decorative plating. The decorative plating can be carried out at the potential ranging from -0.90V to -1.15V, giving the high quality plating. With the different ratio of τ_{Cr} the Cr(III) complex with mono-, di-, triglycine can be formed during plating in the solution. The experiments indicated that the Cr(III) diglycine complex exhibited a more favorable form of discharge at cathode electrode than other forms.

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