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## Electrodeposition of chromium from trivalent chromium urea bath containing sulfate and chloride<sup>①</sup>

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**Abstract:** The reduction of Cr(III) to Cr(II) on copper electrode in trivalent chromium urea bath containing chromium sulfate and chromium chloride as chromium source has been investigated by potentiodynamic sweep. The transfer coefficient  $\alpha$  for reduction of Cr(III) to Cr(II) on copper electrode was calculated as 0.46. The reduction is a quasi-reversible process.  $J-t$  responses at different potential steps showed that the generation and adsorption characteristics of carboxylate bridged oligomer are relevant to cathode potential. The interface behavior between electrode and solution for Cr(III) complex is a critical factor influencing sustained electrodeposition of chromium. The hypotheses of the electro-inducing polymerization of Cr(III) was proposed. The potential scope in which sustained chromium deposits can be prepared is from -1.3 V to -1.7 V (vs SCE) in the urea bath. Bright chromium deposits with thickness of 30  $\mu\text{m}$  can be prepared in the bath.

**Key words:** electrodeposition; chromium; polymerization

**Document code:** A

### 1 INTRODUCTION

To obtain chromium coating by electrochemical procedure, electrodeposition from environmentally friendly Cr(III) bath is more acceptable than that from toxic Cr(VI) (chromium acid) bath. Numerous attempts have been made to deposit chromium from its trivalent state, however, successful applications only limited to thin film (with 1 ~ 6  $\mu\text{m}$  thickness) which only has decorative value<sup>[1~3]</sup>. Meanwhile, because the overpotential of Cr electrodeposition is so great that its electrocrystallization process overlaps on hydrogen evolution reaction (HER), the factors inhibiting sustained electrodeposition of Cr can not be confirmed easily. Watson *et al*<sup>[4,5]</sup> identified the control of transient levels of unstable chromium(II) as the critical factor to make sustained deposition of thick coating of chromium according to indirect experimental data. They considered that the failure of sustained deposition of chromium is due to the generation of oligomeric species of chromium(III), which is

catalyzed by chromium(II). Tu and Yang suggested that failure of sustained deposition was due to sharp increase of pH in diffusion layer<sup>[3]</sup>. However, their results are contrast to the experiment of pH measurement using Brenner drainage technique which proved that pH of diffusion layer reached a steady equilibrium value just under pH 4<sup>[6]</sup>. Unfortunately, most of researchers failed to provide direct evidence of the roles of chromium(II) during electrodeposition due to its unstable nature. Perrin *et al*<sup>[7]</sup> investigated some kinetic parameters and catalytic effect of  $\text{Cr}^{2+}$  in very dilute chromium(III) pure DMF solution which may be different from aqueous electrolyte. With regard to the environmental effects of plating industry, Cr electrodeposition from aqueous electrolyte is more promising than that from toxic organic solvent bath e.g. DMF. The bath using chloride and sulfate as chromium source is more favorite for its lower corrosion to the manufacture equipment than that using chloride only. We have studied aqueous urea bath from which deposits with 30  $\mu\text{m}$

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thickness were prepared without special techniques requirement . In this paper , we report some parameters of Cr( III) / Cr( II) couple and give some novel idea of the electro-inducing polymerization during the deposition process and possible factors hindering continuous deposition of chromium .

## 2 EXPERIMENTAL

The electrolyte was prepared with distilled water and AR grade chemicals according to the composition showed in Table 1 . Urea was chosen

**Table 1** Bath composition

Component	$c / ( \text{mol} \cdot \text{L}^{-1} )$
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	0.40
$\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	0.20
$\text{H}_3\text{BO}_3$	0.40
$(\text{NH}_2)_2\text{CO}$	1.50
Stablizer	0.12
NaCl	0.40
HCOOH	0.40

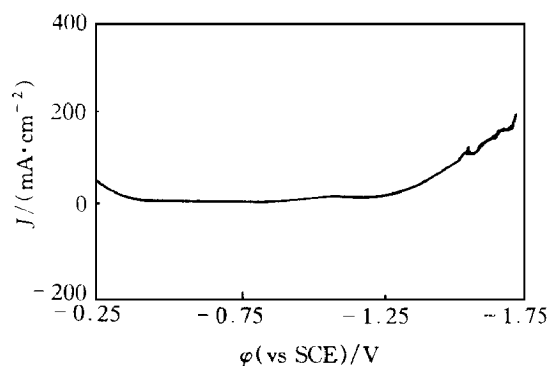
as complexant for its strong donating power due to its resonance structure . Formic acid can act as catalyst for the chromium deposition<sup>[8]</sup> . After preparation , the bath was aged for 48 h and deoxygenated by Ar stream prior to experiments . The working electrode was a copper( 99.99 % purity) disk with a diameter of 1.4 mm . It was degreased with actone , polished with  $\text{Al}_2\text{O}_3$  emery paper gradually from 3 through 1 to  $0.5 \mu\text{m}$  and followed by rinsing with distilled water before experiment . The counter electrode was a Pt plate with an area of  $1 \text{ cm} \times 1 \text{ cm}$  . The reference electrode was saturated calomel(SCE) . An EG & G PARC M273 potentiostat and M270 software was used to carried out cyclic voltammetry , linear sweep and potential steps experiments . The M273 potentiostat was controlled by IBM Pentium computer . The environment temperature was maintained at 298 K . The cross section of deposits was investigated on HI-

TACHI X-650 scanning electron microscope .

## 3 RESULTS AND DISCUSSION

Fig .1 illustrates the cyclic voltammogram for a freshly resurfaced copper microelectrode in the bath . In the absence of chromium sulfate and chromium chloride ,cathodic polarization was carried out in the electrolyte which was adjusted to pH 2.5 . The polarization curve is showed in Fig .2 .

**Fig .1** Cyclic voltammogram for Cu microelectrode ( pH 2.5 , potential scan rate 10 mV/s , temperature 298 K)

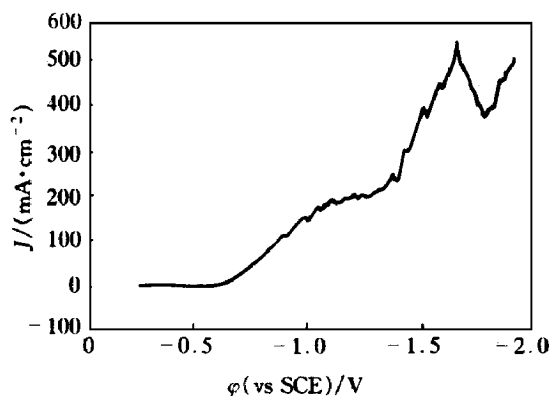


**Fig .2** Cathodic polarization curve in bath without chromium ( pH 2.5 , potential scan rate 10 mV/s , temperature 298 K)

Fig .1 shows there is no current until the electrode potential reaches  $-0.546 \text{ V}$  ,then the

current increases with the sweep going forward. Fig. 2 shows there is almost no current from - 0.55 V to - 1.20 V in the basic bath without trivalent chromium. Because the standard equilibrium potential of reduction of Cr(III) to Cr(II) is - 0.678 V (vs SCE), we regard the current wave labelled A as reduction of Cr(III) to Cr(II).

At the initial phase of wave A, the curve is smooth, but it shows the erratic current response when the potential is more negative than - 0.856 V. The erratic response is due to precipitation or gas evolution in most circumstance. However, because the pH can not increase so quickly that chromium hydroxide precipitates<sup>[6]</sup> and no hydrogen evolution was investigated, we postulate that some species of polymer or olation were absorbed on the electrode which may be generated freshly in diffusion layer or have been existing in the bulk solution. The absorption is relevant to the electrode surface condition. When the cathode potential is more negative than - 1.250 V, the current increases dramatically till the peak at - 1.650 V, which indicates that one or more new electrochemical reactions occurred. The new reactions are HER and the nucleation of chromium metal phase which have the same erratic response. Linear sweep voltammogram in the electrolyte for electrodeposition is showed in Fig. 3.



**Fig. 3** Linear polarization curve in electrolyte for electrodeposition of chromium (pH 2.5, potential scan rate 10 mV/s, temperature 298 K)

Fig. 3 indicates there is a diffusion-limited current in the potential scope from - 1.05 V to - 1.18 V. The average current between - 1.05 V to - 1.18 V is regarded as the limiting current, so,  $J_d$  is equal to 202.7 mA·cm<sup>-2</sup>. Tafel curve in low overpotential scope is showed in Fig. 4. The transformed Tafel equation can be expressed as

$$\varphi = (2.3 RT/ anF) \lg J_0 + \varphi_q - (2.3 RT/ anF) \lg J \quad (1)$$

If electron transfer is the determining step of rate, the relationship of  $\varphi$  vs  $\lg J$  will meet Eqn.(1) and shows the linear nature.

**Fig. 4** Tafel curve of trivalent chromium solution

Fig. 4 shows a good linear relationship between potential and  $\lg J$  ( $R = 0.99936$ ).

According to the slope of Tafel curve, transfer coefficient  $\alpha$  is equal to 0.4582. The linear relationship between potential and  $\lg J$  also indicates that the electrode reaction rate is mainly determined by electron transfer in low overpotential scope. But the Tafel curve deviates linear relationship when the overpotential is out of the section, which indicates the determining step of electrode reaction rate has changed. On the basis of linear polarization curve showing the limiting diffusion current, the electrode reaction rate may be determined by both mass transport and electron transfer steps when the overpotential increases further. Its kinetics will meet the equation

$$\eta_k = (RT/ anF) \ln(J/J_0) + (RT/ anF) \ln[J_d/(J_d - J)] \quad (2)$$

$$\text{or } \varphi = \varphi_q - (2.3 RT/ anF) \lg(J_d/J_0) +$$

$$(2.3 RT/ anF) \lg[(J_d - J)/J] \quad (3)$$

Because  $\varphi_{eq}, J_d$  and  $J_0$  are constant for the definite system under a certain condition, the relationship between  $\varphi$  and  $\lg[(J_d - J)/J]$  will be linear if the reaction rate is governed by both diffusion and electron transfer step.  $\varphi$  vs  $\lg[(J_d - J)/J]$  is plotted in Fig.5.

**Fig.5** Relationship between  $\varphi$  and  $\lg[(J_d - J)/J]$

On basis of the following linear regression  
 $\varphi = -0.78079 - 0.12873 \lg[(J_d - J)/J]$   
 ( $R = 0.9923$ )

the transfer coefficient can be deduced as

$$2.3 RT/ anF = 0.12873$$

$$\alpha = 0.4583$$

The transfer coefficient deduced from the slope of Fig.5 is 0.46 which is very close to the result calculated from Tafel curve. If the reduction of Cr(III) was a reversible process, the relationship between  $\varphi$  and  $\lg[(J_d - J)/J]$  would meet the following equation:

$$\varphi = \varphi_{1/2} + (0.059/n) \lg[(J_d - J)/J] \quad (4)$$

On basis of  $\varphi - \lg[(J_d - J)/J]$  plot and the above equation,  $n$  can be deduced as

$$n = 0.4583$$

Electron transferred is not a integer number, thus the reaction is not reversible.

Fig.6 reports the  $J-t$  response to potentiostatic electrodeposition in which potential

steps from 0 V to -1.2 V, -1.4 V and -1.6 V. Metal chromium can be deposited on copper only after potential is more negative than -1.30 V. The cathodic current maintains steady at -1.2 V, this fact confirms that production of Cr(II) does not change electrode-solution interface greatly. However, when potential steps to -1.6 V the cathodic current increases continuously, which shows electrode reaction resistance decreases with the increase of electrolysis time at this potential. Perhaps HER is catalyzed at -1.6 V, but the reduction of electroactive species of Cr(III) is hindered. Hence, we postulate that some kind of electro-inducing polymerization reaction occurs to generate carboxylate bridged complexes of chromium(III) which interfere with the electrode reaction greatly. Adsorption of these larger oligomers onto the crystal growth site of the metal is believed to cause loss of metallic quality. For example, electrode surface corresponding to  $J-t$  curve in Fig.7 at -1.8 V was covered by a thin layer of brown substance and no any metal chromium was deposited on it. Meanwhile, the decreasing tendency of  $J-t$  curve in Fig.7 also shows that the polymer formed at -1.8 V inhibits not only reduction of trivalent chromium but also inhibits hydrogen evolution by decreasing the diffusion rate of proton in diffusion layer.

**Fig.6**  $J-t$  curve for potential step from 0 V to -1.2 V, -1.4 V, -1.6 V respectively

A possible polymerization model was postur-

lated as below. One of the chromium complex ion of carboxylic substitution may be like  $\text{Cr}[(\text{HCOO})(\text{H}_2\text{O})_5]^{2+}$  which can be absorbed to the electrode for low electronic density of carbon atom. The initiation step of polymerization could be that ligand  $\text{HCOO}^-$  become a radical anion<sup>[9]</sup> which has affinity ability to  $\text{Cr}^{3+}$  of another monomer. Then the polymerization can propagate further. If there are other active ligand, the oligomerization could continue to form trimer, tetramer etc<sup>[10]</sup> through analogous mechanism.

**Fig.7**  $J-t$  curve for potential step from 0 V to -1.8 V

On the basis of previous postulation, the rate of polymerization is improved under the influence of interface electric field, which can affect the structure of oligomer and its relevant nature such as the absorption and desorption characteristics. The further studies related to the electroinducing polymerization is undergoing and will be shown in our later publications.

#### 4 CONCLUSIONS

Reduction of Cr(III) to Cr(II) was detected in the urea bath when potential is more negative than -0.546 V (vs SCE). The kinetics parameter  $\alpha$  is calculated from data of steady state polarization curve as 0.46. The reaction of Cr(III)/Cr(II) couple is a quasi-reversible process. The catalyzing of Cr(III) to the ligand exchange of coordination of Cr(III) can not be defined in our experiment for no clues. Potential steps experiment indicates the polymerization may be relative to electrode interface condition. The structure and nature of oligomer formed on the surface of electrode is strongly relevant to electrochemical factors.

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