



## Role of complexing ligands in trivalent chromium electrodeposition

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### ABSTRACT

In this study, the Cr(III)-formate, Cr(III)-oxalate and Cr(III)-glycine electrolytes are used as sources for electrodepositing the Cr coatings. The deposition rate and brightness range of the electroplating process in these electrolytes are investigated. The geometric structures of the Cr complex ions are optimized, using density functional theory with General Gradient Approximation/Perdew-Wang 91 (GGA/PW91) calculation. It is found that the deposition rate and brightness range significantly depend on the geometric structure of the Cr(III)-ligand complex ions. The expansion of the distance between Cr and H<sub>2</sub>O induced by the introduced complexing ligand is a necessary condition for the electrochemical reduction of Cr(III) to metal Cr. The dehydration rate of Cr(III)-ligand complex ions determines the electroplating characteristics of electrolytes.

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### 1. Introduction

Electroplating technology is widely used in industry and daily life for decoration, anti-corrosion, anti-wear and preparation of metal electrodes [1–3]. Many metals can be electrodeposited from aqueous solutions. In order to obtain high-quality deposits, all kinds of complexing ligands are added into electrolytes. With respect to the Cu, Pb, Zn, Ag, Au, Cd, Pt, Rh, In and Pd plating processes, the complexing ligands, such as CN<sup>-</sup>, sulfamic acid, NH<sub>3</sub> etc. are used to decrease the deposition rate to produce the bright, compact and smooth deposits. While in the cases of Ni, Co and Fe plating processes, the high-quality deposits can be obtained by adding some brighteners instead of complexing ligands. Comparatively, Cr plating process is more complex. Conventional Cr plating is carried out in the hexavalent Cr electrolytes with small amount of H<sub>2</sub>SO<sub>4</sub> or fluoride as catalysts. Due to the toxicity of Cr(VI), now this process is strictly restricted in US, Japan, China, Europe and other areas. Recently, trivalent Cr plating is considered as a promising technology to replace the conventional hexavalent Cr plating. In this plating process, the complexing ligands are also added to the electrolytes, whereas they are used to accelerate the deposition of Cr but not to decelerate it [4,5]. Although complexing ligands obviously promote the electroreduction of Cr(III), they also bring some demerits to the trivalent Cr plating process. For example, thick Cr coating with acceptable quality is hardly obtained from this electrolyte; thus, it is only commercially used for decorative thin Cr electroplating. Nevertheless, the decorative thin Cr coating from trivalent Cr is darker than that from hexavalent Cr, which is unfavorable to the commercial decoration.

Some previous researchers [6,7] tried to investigate the effect of complexing ligands on the characteristics of trivalent Cr plating process in order to improve the trivalent Cr plating technology. But heretofore there are no ultimate opinions on the role of complexing ligands in trivalent Cr plating process because few studies have been conducted at molecular level to explore the essential role of complexing ligands in the electroreduction process of Cr(III).

Generally, in aqueous solution metal ions exist in the form of metal-H<sub>2</sub>O complex ions. The electroreduction reaction of metal-H<sub>2</sub>O complex ions in aqueous solution can be considered as a special nucleophilic substitution reaction that electron replaces H<sub>2</sub>O molecule in aqua metal ions. Electron is a special substituent because it is chained to the cathode. Thus, the geometric structure of metal-H<sub>2</sub>O complex ions plays an important role in the electroreduction. It is a prerequisite for the electroreduction of metal-H<sub>2</sub>O complex ions that metal ions contact the cathodic electrons.

Table 1 summarizes the amount of H<sub>2</sub>O molecules (*n*) and the distance between metal ion and H<sub>2</sub>O (*r*) in different metal-H<sub>2</sub>O complex ions [8]. Ag and Cu can be electroreduced easily from trimolecular structural [Ag(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> and [Cu(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> because metal ions can access and contact the cathode easily. Other metal-6H<sub>2</sub>O complex ions holding the regular octahedron structure with metal ion as a center and H<sub>2</sub>O molecules as vertexes can be divided into two groups. Metal-6H<sub>2</sub>O complex ions with *r* larger than 2.04 Å such as [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> etc. can be electroreduced easily; and those with *r* smaller than 2.04 Å such as [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> etc. can hardly be electroreduced. In fact, metal ions surrounded by six H<sub>2</sub>O molecules cannot contact the cathodic electrons unless H<sub>2</sub>O molecules depart from them firstly. Under the pull of cathodic electrons, metal-6H<sub>2</sub>O complex ions in the former group lose H<sub>2</sub>O molecules firstly to expose metal ions, which is propitious to metal ions that contact the cathode to react with

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**Table 1**

Amount of H<sub>2</sub>O molecules (*n*) and average distance between metal ion and H<sub>2</sub>O molecule (*a-r*).

Metal ion	Al <sup>3+</sup>	Cr <sup>3+</sup>	Fe <sup>3+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sup>2+</sup>	In <sup>3+</sup>	Mn <sup>2+</sup>	Cd <sup>2+</sup>	Ag <sup>+</sup>	Cu <sup>2+</sup>
<i>n</i>	6	6	6	6	6	6	6	6	6	6	2	2
<i>r</i> (Å)	1.90	2.00	2.00	2.04	2.08	2.08	2.12	2.15	2.20	2.31	2.41	2.43

cathodic electrons. On the other hand, with respect to metal-6H<sub>2</sub>O complex ions in the latter group, the dehydration can hardly occur, and metal ions are unable to contact cathode to react with cathodic electrons. It should be pointed out that Al can be electrodeposited from ionic liquids based on AlCl<sub>3</sub> and organic halide [9] because no [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ions are formed in ionic liquid electrolytes. Thus, it can be confirmed that the dehydration is a necessary condition for the electroreduction of metal-6H<sub>2</sub>O complex ions. And the distance between metal ion and H<sub>2</sub>O of metal-H<sub>2</sub>O complex ions determines their ability to lose H<sub>2</sub>O molecules.

It is important to note that the electroreduction of Cr(III) is special in respect that Cr can deposited from [Cr(H<sub>2</sub>O)<sub>6-x</sub>L<sub>x</sub>]<sup>3-x</sup> (L, complexing ligand) rather than [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. Thus, the investigation on the role of geometric structure in the electroreduction of Cr complex ions is important both for the improvement in trivalent Cr electroplating and for the development in theory of metal ions electrodeposition in aqueous solution.

J. Szynekarczuk et al. [10,11] have studied the electrochemical behaviors of trivalent Cr in the presence of formic acid. They thought the electroreduction of Cr complex ions underwent two electrochemical processes. The first one is responsible for electroreduction to bivalence Cr when the other to metallic chromium, whereas they did not elucidate the essential role of formic acid during the electroreduction. In our previous work [4], we have investigated the effects of formate on the electroreduction of trivalent Cr by analyzing the geometric structures of the Cr(III)-ligand complex ions. It is found that the formate replaces H<sub>2</sub>O molecule in Cr(H<sub>2</sub>O)<sup>3+</sup> to expand the distance between Cr<sup>3+</sup> and H<sub>2</sub>O, which expedite the dehydration to accelerate the electroreduction of trivalent Cr to bivalence Cr. When Cr<sup>3+</sup> ion obtains an electron, the Cr complex ion becomes [Cr(H<sub>2</sub>O)<sub>4</sub>CHOO]<sup>+</sup> which exhibits a very large *r* value. In this case, all H<sub>2</sub>O molecules are easy to depart from central Cr<sup>2+</sup> and the further electroreduction of Cr<sup>2+</sup> will proceed quickly. Nevertheless, there are still some essential issues which are valuable to be further discussed. For example, are the effects of ligand on the electroreduction of Cr(III) in other trivalent Cr electrolytes such as Cr(III)-oxalate and Cr(III)-glycine systems also attributed to the change in the geometric structures? Why do the properties of ligands and molar ratio of Cr to ligand affect the electroplating characteristics of electrolytes? And why can the thick Cr coatings with acceptable quality hardly be obtained from Cr(III)-formate electrolyte in the commercial operation?

In this work, we investigate the equilibrium geometric structures of Cr(III)-ligand complex ions, brightness range and deposition rate in three different electrolyte systems. Cr(III)-formate, Cr(III)-oxalate and Cr(III)-glycine electrolyte systems are selected because they are popularly used both for academic research and for commercial

operation. The final aim is to establish a systemic theory of trivalent Cr electroplating, which may provide some valuable information both for trivalent Cr electroplating and for the electrodeposition of other metal from aqueous solutions.

## 2. Experimental

### 2.1. Bright range measurement

The chemical components of electrolytes are summarized in Table 2. Electrolytes were boiled for 1 h in order to promote the ions reach equilibrium state, and then NaOH solution was used to adjust pH value to 3.0. To achieve the final thermodynamic equilibrium state, the solutions were placed for 30 days before the electrodeposition. The final pH value of solutions needs to be adjusted to 3.0 in order to ensure the accuracy of following measured results. "Hull cell" of 267 ml was used as the plating bath, dimensionally stable titanium plate (Xinxiang Future Hydrochemistry Co., China) and copper were used as the anode and cathode, respectively, and the electrodeposition was conducted with the current of 6 A at 30 °C for 2 min. The length of bright Cr-covered area was measured to determine the bright range. The corresponding current density was evaluated by the experimental equation (German Criterion DIN50957) expressed as

$$D = I(510.19 - 524.01 \lg L / 10)$$

where *I* is the total current density in A m<sup>-2</sup>, *D* is the current density at the certain position (A), and *L* is the distance between A and the edge of the cathodic copper in mm.

### 2.2. Deposition rate test

Copper substrate with areas of 0.04 dm<sup>2</sup> was used as cathode. In order to obtain the even coating on the substrate, the electrodeposition was carried out in the bath of 5000 ml with graphite plate as the cathode. The deposition rate was determined by measuring the quality difference between coating-covered substrate and blank substrate.

### 2.3. Geometric structure analysis

Geometric structural conversion of Cr complex ions in electrolytes was analyzed by means of GGA/PW91 calculation which is widely used for optimizing the geometric structure of compounds [12,13].

## 3. Results and discussion

Fig. 1 shows the bright range of the copper after "Hull cell" experiment in different electrolytes. Bright Cr coatings are obtained in the Cr(III)-formate electrolytes with the current density ranging from 4 A dm<sup>-2</sup> to 57 A dm<sup>-2</sup>. And it seems that the molar ratio of Cr to formate does not affect the bright range. Comparatively, the bright range is significantly affected by the molar ratios of Cr to oxalate and Cr to glycine. The bright range is from 10 A dm<sup>-2</sup> to 60.5 A dm<sup>-2</sup> for

**Table 2**

Component of electrolytes.

Reagent	1) Cr-formate (1:1) mol l <sup>-1</sup>	2) Cr-formate (1:2) mol l <sup>-1</sup>	3) Cr-oxalate (1:1) mol l <sup>-1</sup>	4) Cr-oxalate (1:2) mol l <sup>-1</sup>	5) Cr-glycine (1:1) mol l <sup>-1</sup>	6) Cr-glycine (1:2) mol l <sup>-1</sup>
Cr <sup>3+</sup>	0.6	0.6	0.6	0.6	0.6	0.6
NaCl	1	1	1	1	1	1
HCOOH	0.6	1.2				
HOOCOOH			0.6	1.2		
H <sub>2</sub> NCH <sub>2</sub> COOH					0.6	1.2
AlCl <sub>3</sub>	0.5	0.5	0.5	0.5	0.5	0.5

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