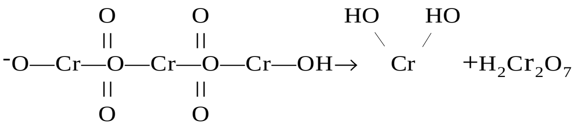
Chemistry & Theory of Chromium Deposition: Part II—Theory of Deposition

By N.V. Mandich

In Part II, various theories of chromium electrodeposition, based on wide-ranging research, are discussed, and an effort is made to show the complexity of chromium deposition and that it is still not completely understood. Part I was published in the May 1997 issue of *P&SF*.

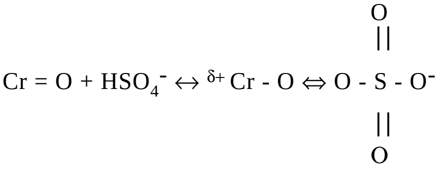
The dominant role of trichromates in chromium deposition is advanced by Hoare.[38] According to his phenomenological model, in the absence of the bisulfate ion (or sulfate, which at low pH dissociates to bisulfate), trichromate ion in successive steps (of electron transfer and loss of oxygen and reaction with H_3O^+ ion) will decompose, as in Eq. (25), to chromous hydroxide and dichromates that may undergo condensation with other chromates to regenerate trichromates. The process then includes an intermediate step of formation of chromic (+3), then chromous (+2) dichromates, finally discharging at the cathode as black chromium at very low current efficiency. Those steps are briefly described below.



$$ {}^{-}O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}—O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}—O—Cr—OH \rightarrow \overset{HO\diagdown\quad\diagup HO}{Cr} \quad + H_2Cr_2O_7 \qquad (25)$$

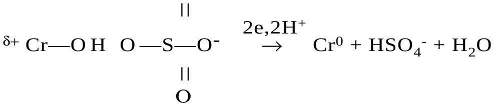
The next step of the reduction mechanism is the formation of a complex between the Cr^{+2} hydroxide and the bisulfate through hydrogen bonding:

$$Cr\,(OH)_2 \Leftrightarrow Cr{=}O + H_2O \qquad (26)$$



$$Cr = O + HSO_4^- \leftrightarrow {}^{\delta+}Cr - O \Leftrightarrow O - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O^- \qquad (27)$$

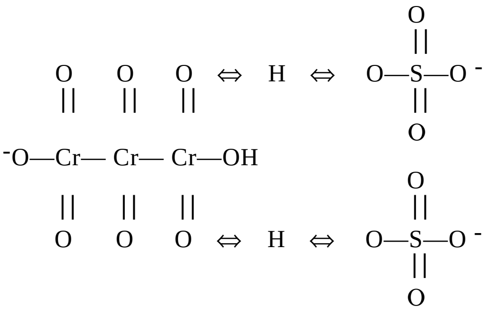
where ⇔ represents the hydrogen bond and δ+ represents a dipole generated on the chromium end (left side) of the complex. Now, the positively charged complex can be specifically adsorbed on the cathode, two electrons transferred to this end-on configuration with formation of metallic Cr and regeneration of HSO_4^-:



$${}^{\delta+}Cr—O\,H \quad O—\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}—O^- \xrightarrow{2e,2H^+} Cr^0 + HSO_4^- + H_2O \qquad (28)$$

According to this model, the chromic-dichromate complex is necessary to protect Cr^{+3} from forming the stable Cr(III) aquo complexes. As a refinement of this model, HSO_4^- ion has a dual role—it also "blocks" other chromium atoms in the trichromate ions from being reduced (leading to Cr^{+3} aquo-complexes formation).

The ideally protected trichromate ion would be:



$$\begin{array}{ccccccc} &&&&&& O\\ &&&&&& \|\\ O & O & O & \Leftrightarrow & H & \Leftrightarrow & O—S—O^-\\ \| & \| & \| &&&& \|\\ &&&&&& O\\ {}^{-}O—Cr— & Cr— & Cr—OH &&&& \\ &&&&&& O\\ \| & \| & \| &&&& \|\\ O & O & O & \Leftrightarrow & H & \Leftrightarrow & O—S—O^-\\ &&&&&& \|\\ &&&&&& O \end{array} \qquad (29)$$

This would leave one end [the right side of (29)] protected, preventing formation of unwanted dichromic chromate complex, decomposition of which would lead to unwanted $[Cr(H_2O)_6]^{+3}$ formation. This also explains the narrow range (CrO_3:HSO_4 = 100:1) of bisulfate concentration in the chromium plating solution; too little HSO_4^- will cause insufficient protection of Cr on the right end of the trichromate ion (under-catalyzation); too much would block the left end Cr, which is necessary for reactions (25)-(28) and Cr deposition (over-catalyzation).

According to Hoare,[39] for fluoride-catalyzed CrO_3-based plating systems, almost the identical mechanism is proposed in which F^- plays the role of blocking agent and catalyst. Although not complete, this mechanism is the most recognized to date. The incompleteness of his remarkable theory is that it treated the chromium deposition mechanism without elaboration on the structure of and influence of the liquid layer adjacent to the cathode (L-film), which is formed at the beginning of the cathodic process and is continuously forming and reforming in the steady-state condition.

Both older and newer Russian research is extensive on the L-film formation and reactions that occur in the film. They quite early recognized its decisive importance for the deposition mechanism in general and for current efficiency in particular.

On the other hand, it is a well-known fact that halide ions (X) such as Cl^- and F^- have a marked improving effect on the cathode current efficiency of chromium electrodeposition as recently reported.[40]

Because the hydration of halide anions is incomplete, they can penetrate the hydrogen layer and be absorbed onto the metal surface. XPS results show that F^- and Cl^- ions, which are stable in the chromic acid bath, may participate in the film formation. The probable activation steps of halides are as follows—the absorbed halide first penetrates the hydrogen layer at the chromium surface and forms a bridged transition surface complex:

$$[Cr_2O_7\,(H_2O)_2Cr^{+3}\text{-}X^-\text{-}Cr^{+3}\,(OH_2)_2Cr_2O_7]^{+2} \qquad (30)$$

The electrons on the cathode are transferred to Cr^{+3} through halides, and Cr^{+3} is reduced to metallic chromium. By the formation of the transition complex, the activation energy of the reduction of Cr^{+3} to Cr^0 is decreased. The overpotential of chromium deposition apparently is decreased, which facilitates chromium electrodeposition.

The rate of reaction follows a first order rate equation.[41] In the case of a rotating cylinder, the specific reaction rate constant was found to increase with increasing rotation speed until a limiting value was reached with further increase in the rotation speed. A study of the reaction mechanisms has shown that, at a relatively low rotation speed, the reduction of chromium is partially diffusion-controlled; at higher speeds, the reaction becomes kinetically controlled. Agitation (cylinder rotation) increases the rate of chromium reduction by decreasing the degree of cathode coverage by hydrogen bubbles, consequently increasing the effective cathode area.[42,43]

In this sense, it seems that non-stationary currents can be of great advantage, because the current interruptions and/or current reversal can promote hydrogen liberation. Also, the use of current pulses interrupts the nucleation and resulting crystal growth. Each pulse yields room for fresh renucleation with the net effect of refining the structure and size of grains. Grain consolidation appears to interfere with the accumulation of internal stresses and to act as an inhibitor of crack formation, as noted in earlier studies.[44]

As reported in a recent paper,[32[Part I]] an x-ray diffraction study was done to identify the predominant species in an industrial CrO_3-H_2O system. Structural analysis showed that dichromate ions have maximum likelihood, but that linear trichromate ions may also exist in significant concentrations. This study also concluded that formation of a complex shown in Eq. (29) can be hardly assumed, because of steric hindrance and that it is more realistic that one HSO_4^- ion reacts with polychromate.

A very recent paper[45] by Russian researchers studied the existence of various chromium complexes in CrO_3/H_2SO_4 plating solutions for different $X = CrO_3/H_2SO_4$ ratios. They concluded that although five different chromium complexes exist, the reduction to metal proceeds only from the following type of complexes:

$$[\,HSO_4\,]n^-\cdot[\,Cr_2O_7\,]m^{-2} \qquad (31)$$

where $n = 1$, $m = 1$ and $25 < X < 150 - 200$.

They concluded that those complexes are characterized by a single hydrogen bond between two ions in the complex.

Another recent paper on chromium mechanisms is the latest contribution of a group headed by Z.A. Soloveva[46] from the Institute of Physical Chemistry of the Russian Academy of Science. Potentiodynamic and impedance measurements are used to further corroborate their mechanism of deposition, based on formation of a cathode film (with solid and liquid phases), consisting of oxide-hydroxide Cr^{+3} compounds. A few other Russian groups headed by Professors Shluger, Vargamyan, Levin, Kudryavtsev, Matulis, and Falicheva, among others, contributed a significant amount of research, but the problem of a final and definite answer is still open. It is clear at this point that for a successful approach and significant further contributions, an *in situ* method is needed to study the deposition mechanisms under both transient and steady state conditions.

Pressure from environmentalists is stirring new research for replacing Cr^{+6} solutions by the less toxic Cr^{+3}. At the same time, it becomes obvious that mechanisms of deposition from trivalent and hexavalent solutions are thoroughly intertwined and that, in both cases, chromium coordination chemistry is heavily involved.

Despite the flurry of research on chromium deposition mechanisms in the 1950s, 1960s and 1970s, the flow of papers on chromium was reduced to a trickle. The reason is obvious—the complexity of the problem and the difficulties involved with highly colored, highly concentrated solutions of chromium salts, the number of different valence states involved, and general lack of in-depth knowledge of chromium coordination chemistry.

What further complicated the matter is that at the (onset) of the deposition process (the first 1-3 sec), one set of reactions occurs—formation of the film, more or less compact and independent of the anions present and rather thin (5 mg/m^2). Russian workers use the term “product of partial reduction of $Cr^{+6} \longrightarrow Cr^{+3}$,” and this film forms in the first branch of the chromium polarization curve, at potentials up to about 700 mV, as shown in Fig. 5. Once this film is formed (the C-film, short for compact film), another cathodic film (layer) is formed on the surface of the C-film and closer to the bulk of the solution—the L-film (short for liquid film).

Significant Japanese contributions toward explanation of these mechanisms unfortunately passed largely unnoticed as a result of language barriers. Because of their apparent importance, a review follows.

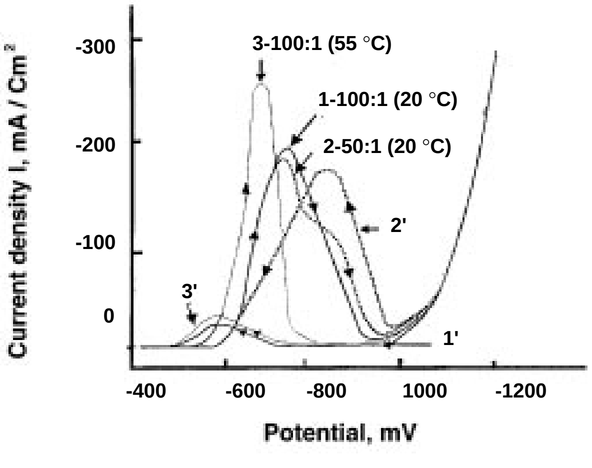


Fig. 5—Linear Cyclic Polarization potential scans for chromium cathode in Sargent bath with 100:1 (1-1') and 50:1 (2-2') ratios at 20 °C, and 50:1 (3-3') at 55 °C. Scan rate v = 142 mV/sec.

Japanese School of Thought On Chromium Deposition Mechanisms

Yoshida, Suzuki, Doi and Arai[47] studied the behavior and composition of a cathode film with the help of radioactive tracers in the form of S^{35} radioactive-labeled sulfuric acid and over-the-counter, high-grade CrO_3, treated with radiation to obtain Cr^{51} as a tracer. A special, rather simple plating cell was constructed with a rapid rinsing station. In essence, a steel cathode was plated for a short time, so that the C- and/or L-films were formed and could be analyzed. Because the L-film is liquid and soluble in either hot plating solution or hot alkali, by dissolution or simple brushing, its formation and influence on the deposition of metallic chromium was studied. By initially forming the C- and L-films with radioactive-labeled Cr or H_2SO_4, and plating in pure (unlabeled) solution and vice versa, they came to these important conclusions:

1. The cathode film is composed of two layers with different forming properties in terms of thickness and composition. The outer layer, referred to as the L-film, and the inner layer, the C-film, differ in that the L-film contains sulfate ions and dissolves easily in the electrolyte and is about 10 times thicker than the C-film.
2. The C-film has a mass of about 5 mg/m^2, contains very few sulfate ions and does not dissolve easily in the electrolyte.
3. The cathode film itself is not reduced to metallic chromium, which is deposited from a separate chromium complex compound that passes through the cathode films (C and L) from the bulk of the solution.
4. In the electrolyte, the L-film vigorously repeats the dissolving and forming cycles, while the C-film remains constant, once formed.
5. The cathode film may be a chromium hydroxy *aquo* complex, as shown in Fig. 6, or primarily an oxolated version of this compound. Assuming that the cathode film is formed from such chromium complexes, the authors suggest that the L-film is a compound with lower molecular weight, such as in structures (i) and (ii), while the C-film is more like structure (iv), a large complex with a high degree of polymerization.

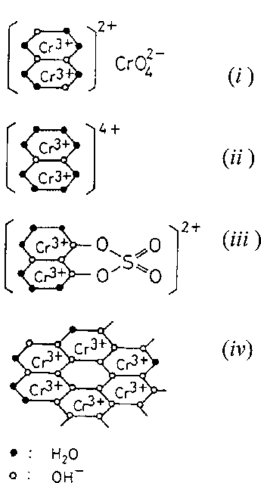


Fig. 6—Structures of chromium complexes in cathode film layer.

Kimura and Hayashi[48] also used sulfates labeled with radioactive S^{35} to overcome the difficulties of determining the amount of sulfate in the cathode film by standard analytical methods (because of its relatively small content) and to study sulfate content in the cathodic film formed during potentiostatic polarization of 0.4, 1.5 and 2.5 M CrO_3 baths on Fe, Au and Pt cathodes. They found that sulfate content is directly related to the potential in the region of -0.6 to -1.0 V, which in turn is controlling the state of the cathode surface (L-film formations) and accompanying electrochemical reactions. In the region of -0.2 to -0.8 V, where current is increasing (C-film), sulfate content was negligible for Pt, Au and Fe cathodes. In the region > -0.8 V, where current starts to decrease and L-film starts to form, sulfate concentration increases sharply. In the potential regions between -1.0 and -1.1 V (beginning of Cr deposit region), sulfate concentration in the film drops as a result of liberation of sulfates from the complexes. At potentials of > -1.1 V, sulfate concentration increases slightly again because of inclusion in the cracks and imperfections in metallic chromium deposits. They also found that as sulfate concentration in a 0.4 M CrO_3 bath is increased from 0.002 M (200:1) to 0.008 M (50:1), sulfate content in the L-film tended to increase. Temperature increase has a similar effect, while an increase in CrO_3 concentration at constant ratio has the opposite effect. At every CrO_3 concentration, the maximum amount of sulfates in the L-film is predictably at 100:1 ratio of sulfuric acid. The authors also investigated the influence of other anions in addition to H_2SO_4; HCl or KBr (0.01 M) added to 1.5 M CrO_3 + 0.01 M H_2SO_4 solution considerably increased the sulfate content of the L-film, while 0.01 M Na_2SiF_6 addition had the opposite effect, demonstrating the substantial film dissolution effect of Na_2SiF_6. The effects of HCl, KBr and Na_2SiF_6 on the film were also proportional to increases in their respective concentrations.

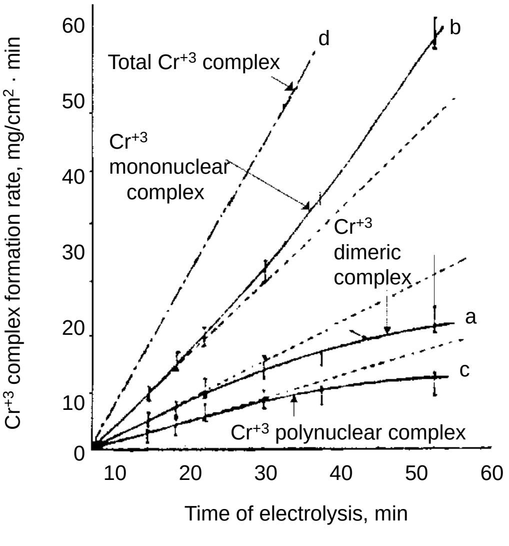


Fig. 7—Formation rates of Cr^{+3} complexes.

Nagayama and Izumitani[49] studied the coordination chemistry of chromium complexes as related to deposition mechanisms. They started with observations made by Levitan[50] that during galvanostatic (I = 75 mA/cm^2) chromium deposition from a sulfate-catalyzed bath, a chromic acid dimer of the type like that in Eq. (11) is formed together with a polymer of unknown structure, as well as mononuclear $[Cr(H_2O)_6]^{+3}$, the stable *aquo* complex. Rather than use the galvanostatic method, where current is kept constant and potential changes, they chose to keep potential fixed at -0.75 V (vs. SCE), where only Cr^{+6} —> Cr^{+3} and $2H^+$ —> H_2 reactions are in progress (for the Cr^{+6} —> Cr^{+3} reaction to happen, this potential is too positive). During electrolysis (0-60 min), they took samples at different time intervals and, with the use of anion and cation exchange chromatography, they separated mononuclear (b) binuclear (a) polynuclear, Cr^{+3} complexes (c). Their formation rates are shown in Fig. 7 and reproduced from their paper. They found that the complex formation rate for mononuclear complexes increases linearly with time, while for the other two complexes, the rate increase is more gradual. Because formation rates were straight lines (at least at the beginning), they can be expressed as the corresponding slopes. Noting that the sum of the slopes for lines a, b and c add up to the slope of line d (total Cr^{+3}-complex formation line), they concluded that each complex is forming at its own constant rate. For complexes a, b, and c, they found the growth rates to be: 0.90, 0.519, and 0.311 mg/cm^2/min, respectively. After the completion of the electrolysis, the binuclear and polynuclear complexes were found to be decomposing to monomers in the absence of the current.

By measuring the decomposition rates, of a, b and c complexes, they found that the overall decomposition rate is first order and can be expressed as:

$$\frac{dC}{dt} = r - kC \tag{32}$$

After integration they obtained:

$$C = \frac{r}{k}\left(1 - e^{-kt}\right) \tag{33}$$

where

C is overall decomposition rate of binuclear or polynuclear complexes,

r is formation rate (slopes of dashed lines from Figure 6),

k is decomposition rate constant and t is time of electrolysis

They repeated the experiment at -1.10 V (Cr^0 formation region) and obtained similar results. The authors concluded in this rather important paper that the cathode layer, consisting of the dense film of various Cr^{+3}-complexes, is a necessary condition for deposition reaction $Cr^{+6} \rightarrow Cr^{+3} \rightarrow Cr^{+2} \rightarrow Cr^0$ to happen. The catalyst (*e.g.*, H_2SO_4) promotes formation and dissolution of binuclear and polynuclear soluble Cr^{+3} complexes, thus maintaining a film of constant thickness where deposition proceeds via intermediate Cr^{+2} (inner orbital) complex rather than through the extremely stable $[Cr(H_2O)_6]^{+3}$ (outer orbital) complex.

Nagayama and Izutami have also assumed that the $Cr^{+3} \rightarrow Cr^{+2}$ step is reduction within the cathode film. Cr^{+2} reacts with a polynuclear hydroxy *aquo* complex, and that portion of the Cr^{+2} obtained in this way reacts with Cr^{+6} and is oxidized to Cr^{+3} ($Cr^{+2} + Cr^{+6} \rightarrow 2Cr^{+3}$), with the remainder being reduced to metallic chromium.

Okada[51] holds that SO_4 ions will penetrate an olated compound, such as that shown in Fig. 6 as structure (iv) to form a complex, such as that in structure (iii), and that from this complex metallic chromium is deposited. According to Okada, reduced solubility of the L-film causes the OH cross-linking level to rise together with the increase in pH.

Yoshida, Tsukahara and Koyama[52] used ESCA to further elaborate their previous research, in which they noted that there are two layers, the L- and C-films, within the cathode film. They obtained depth profiling of these films and demonstrated the C-film is a highly polymerized complex, with very few anions present, if any. The L-film appears to be mostly in the Cr^{+3} state, but the exact valence could not be accurately established, suggesting the possibility of two- and four-valence states also.

They suggested that Cr^{+3} complexes are the main constituents of L-film and that metallic chromium does not deposit from this cathode film, but from the Cr^{+6} state, which contributes to the formation of the cathode film, but also forms olated complexes, hydroxy *aquo* complexes and polymers of higher molecular weight. These olated complexes will penetrate the cathode film from the bulk of the solution before being reduced to metallic chromium.

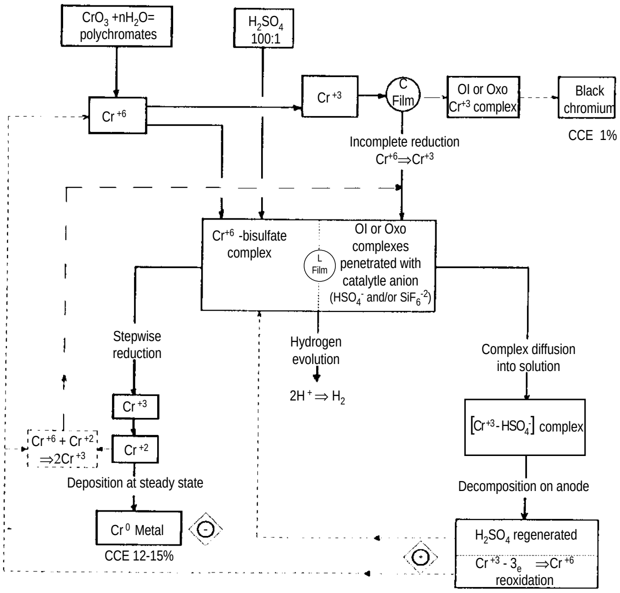


Fig. 8—Proposed sequences of the mechanism of chromium deposition.

Nishihara *et al.*[53] studied Cr^{+3} complexes and the reaction $Cr^{+3} + e^- \rightarrow Cr^{+2}$ as related to pH and temperature, using the aqueous solution of chrome alum: $[(NH_4)Cr(SO_4)_2 \cdot 12H_2O]$. As the temperature of the chrome alum solution is raised from room temperature to 80 °C, the pH of the solution decreases proportionately with the temperature. The half-wave of the $Cr^{+3} + e^- \rightarrow Cr^{+2}$ reaction moves toward more negative potentials and the reaction changes from reversible to irreversible with the color of the solution changing from violet to green. From these results, it is postulated that the degree of hydrolysis of Cr^{+3} complexes is temperature dependent. The structures of Cr^{+3} *aquo* complexes are estimated (at > 40 °C), as $[Cr(H_2O)_6]^{+3}$ and $[Cr(H_2O)_5OH]^{+2}$; at 40 to 70 °C as

$[Cr(H_2O)_5OH]^{+2}$, $[Cr(H_2O)_4(OH)_2]^+$ and olated polymers, as represented in Eq. (11); and at > 80 °C, mostly as olated polymers, such as in Eq. (11).

Summary

The whole complex problem is centered on the exact mechanism that can, for reasons of clarity, be described in Fig. 8, noting again that this is a simplification of one complicated mechanism that happens in different steps and that electrochemically and kinetically, is still poorly understood. Explanation of CrO_3 electrodeposition mechanisms will undoubtedly benefit closely related fields, such as electrodeposition from trivalent decorative and hard chromium plating baths, as well as chromium conversion coatings.

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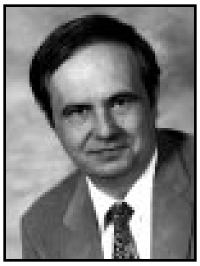

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