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CHEMISTRY OF CHROMIUM

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ABSTRACT

Chromium is technologically and ecologically a very important element. Still it is difficult to find in one place enough details about its chemistry in relation to electrodeposition. An attempt is made to present its stereochemistry, electrochemistry, redox reactions and structure of polynuclear chromic acids, among others. Present status of chromium deposition mechanisms in relation to chemistry involved is detailed a fundamental and contemporary point of view.

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CHEMISTRY OF CHROMIUM

Chromium, Cr, also loosely called Chrome, is the twenty-first element in relative abundance with respect to the earth's crust, yet is the seventh most abundant element because Cr is concentrated in the earth's core and mantle. It has atomic number 24 and belongs to the group 6(VI B) of the Periodic Table. On a tonnage basis, chromium ranks forth among the metals and thirteenth of all mineral commodities in commercial production.

Chromium was discovered by Vauquelin in 1779 in Siberian red lead, the mineral *Crocoite*, $PbCrO_4$. In 1798 he isolated the new metal by reduction of CrO_3 with charcoal at high temperature. The name chromium (from Greek *chroma*, color) was suggested for the new element because of its many colored compounds. Chromium , relatively recently, is recognized as a biologically necessary trace element. The first conclusive evidence demonstrating a metabolic role for chromium was obtained by Mertz and Schwartz[1] in a series of investigations the first of which appeared in 1955.

Chromium has a ground state electronic configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ $3d^5$, $4s^1$. This distribution of the outermost electrons is favored over $3d^4$ $4s^2$ because of increased stability of the half-filled 3d shell with 1 electron in each of the orbitals. The half-filled shell leads to "S" state (L=0) which are especially stable supposedly because of the large amount of exchange energy[2] . The *d* orbital project close to the surfaces of the ions so that the electrons in them interact with the chemical environment.

A typical transition element, chromium forms many compounds that are colored and paramagnetic. Chromium has oxidation states as follows: 2^-, 1^- , 0, 1^+, 2^+, 3^+ , 4^+, 5^+, 6^+; the highest oxidation state, 6^+ , corresponds to the sum of the numbers of 3*d* and 4*s* electrons. The lowest 2^-, 1^- , 0 and 1^+ are formal oxidation states displayed by chromium in compounds such as carbonyls, nitrosyls and organometalic complexes.

DIVALENT CHROMIUM

Chromium in the oxidation state 2^+ is not of particular great interest for electrodeposition mechanisms . However, it does play a role in passivation of chromium and also recently it is accepted that possibly plays a role in deposition and dissolution mechanisms; this warrants that it be briefly introduced here.

The outstanding characteristics of the Cr^{2+} ion (sky blue in aqueous solution) is its strength as a reducing agent $Cr^{3+} + e \rightleftharpoons Cr^{2+}$; $E_0 = 0.41$ V. Since it is easily oxidized by oxygen , preservation of solution requires exclusion of air. Even under such conditions, the Cr^{2+} ion is oxidized by water with the formation of hydrogen. The rate of oxidation depends of several factors, including the acidity and the anions present

It has been known for some time[3], that pure chromium (usually obtained electrolyticaly) dissolves in acids to form Cr^{2+} with no (or very little) Cr^{3+} , (if the solution is protected from air, of course); impurities apparently catalyze formation of Cr^{3+} . Chromium (2+) solutions may also be obtained by electrolytic reduction of Chromium (3+)4,5 . Recently Leisner[6] proposed chromium dissolution mechanism during anodic dissolution of chromium in chromium plating solution, postulating $Cr^0 \rightarrow Cr^{2+}$ oxidation under these conditions,. Mandich[7] also studied anodic dissolution of chromium in 240 g/l CrO_3 + 2.4 g/l H_2SO_4 solution using Weight difference, Voltametry and Quartz Crystal Microbalance methods under different current densities and temperatures. He found that anode current efficiencies for all three methods were in the 104 - 109% range, if calculated for $Cr^0 \rightarrow Cr^{6+} + 6e$ reaction, indicating that at least two electrochemical reactions are involved and perhaps a chemical reaction. Interesting is the detail that dissolution rate is about the same with or without sulfate, which is opposite for chromium deposition mechanism. A study is in progress to elucidate the exact mechanism with the help of a ring-disc rotating gold electrode.

Dissolution of chromium in acid media (mostly H_2SO_4) is examined quite extensively in corrosion studies of chromium metal and alloys. Active dissolution yields chromous ions according to the most of the models[8-9] while the active-passive transition is associated with the formation of the blocking passive layer.

TRIVALENT CHROMIUM

Chromium (3+) is the most stable and most important oxidation state of the element. The E^0 values (Table 1) shows that both the oxidation of Cr^{2+} to Cr^{3+} and the reduction of Cr^{6+} to Cr^{3+} are favored in acidic aqueous solutions. The preparation of Cr^{3+} compounds from either state presents few difficulties and does not require special conditions. In basic solutions, the oxidation of Cr^{3+} to Cr^{6+} by oxidants such as peroxides and hypohalites occurs with ease. The preparation of Cr^{6+} from Cr^{3+} in basic solutions requires the use of powerful reduction agents such as hydrazine, hydrosulfite and borohydride, but Fe^{2+}, thiosulfate and sugars can be employed in acid solutions.

Half cell reaction	E^0 ,V
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
$Cr(OH)^{2+}\ H^+ + 3e^- \rightarrow Cr + H_2O$	-0.058
$Cr^{2+} + 2e^- \rightarrow Cr$	-0.91
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$Cr_2O_7^{2-} + 10H^+ + 6e^- \rightarrow 2Cr(OH)_2 + 3H_2O$	1.10
$CrO_4^{2-} + e^- \rightarrow CrO_4^{-3}$	0.1
$Cr^{6+} + e^- \rightarrow Cr^{5+}$	0.6
$Cr^{5+} + e^- \rightarrow Cr^{4+}$	1.3
$Cr^{4+} + e^- \rightarrow Cr^{3+}$	2.0

Table 1. Standard Reduction Potentials for Chromium Species[25]

Reaction	Log *K*
$Cr^{2+} + H_2O \rightleftharpoons Cr(OH)^+ + H^+$	5.3
$Cr^{3+} + H_2O \rightleftharpoons Cr(OH)^{2+} + H^+$	-4.2
$Cr^{3+} + 2\,H_2O \rightleftharpoons Cr(OH)_2 + 2\,H^+$	-10.4
$Cr^{3+} + 3\,H_2O \rightleftharpoons Cr(OH)_3 + 3\,H^+$	-18.7
$Cr^{3+} + 4\,H_2O \rightleftharpoons Cr(OH)_4 + 4\,H^+$	-27.8
$2\,Cr^{3+} + 2\,H_2O \rightleftharpoons [Cr_2(OH)_2]^{4+} + 2\,H^+$	-5.3
$3\,Cr^{3+} + 4\,H_2O \rightleftharpoons [Cr_3(OH)_4]^{5+} + 4\,H^+$	-8.7
$4\,Cr^{3+} + 4\,H_2O \rightleftharpoons [Cr_4(OH)_6]^{6+} + 6\,H^+$	-13.9
$Cr^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Cr(C_2O_4)_3]^{3-}$	-15.4
$Cr^{3+} + H_2\,EDTA^{2-} \rightleftharpoons [CrEDTA]^- + 2\,H^+$	23.4
$Cr^{3+} + SO_4^{2-} \rightleftharpoons Cr\,SO_4^+$	1.8
$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$	0.61
$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$	-5.9
$2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$	2.2
$H_2CrO_4 + Cl^- \rightleftharpoons CrO_3\,Cl^- + H_2O$	1.0
$HCrO_4^- + HSO_4^- \rightleftharpoons Cr_2\,SO_7^{2-} + H_2O$	0.60

Table 2. Hydrolysis, Equilibrium, and Complex Formation Constants

The chemistry of Cr^{3+} in aqueous solutions is coordination chemistry. It is demonstrated by the formation of kinetically inert octahedral complexes.

The bonding can be explained by $d^2\,sp^3$ hybridizations and literally thousands of complexes have been prepared. The kinetic inertness results from the $3d^3$ electronic configuration of Cr^{3+} ion[12]. This type of orbital charge distribution makes liquid displacement and substitution reactions very slow and allows separation, persistence and /or isolation of Cr^{3+} species under thermodynamically unstable conditions.

Hydrolysis of Chromium (3+) and related Processes.

Chromium (3+) is characterized by a marked tendency to form polynuclear complexes. Literally thousands of Cr^{3+} complexes have been isolated and characterized and with a few exceptions, are all hexacoordinate. The principal characteristic of these complexes in aqueous solution is their relative kinetic inertness. Ligand displacement reactions of Cr^{3+} complexes have half-times in the range of several hours. It is largely because of this kinetic inertness that so many complex species can be isolated as solids and that they persist for relatively long periods of time in solution even under conditions of marked thermodynamic instability.

The hexaaqua ion $[Cr(H_2O)_6]^{3+}$, which is a regular octahedral, occurs in numerous salts such as the violet hydrate $[Cr(H_2O)_6]Cl_3$ and in an extensive series of alumns $MCr(SO_4)_2 \cdot 12\,H_2O$

The aqua ion in acidic (pK = 4), and the hydroxo ion condenses to give dimeric hydroxo bridged species:

$$\left[Cr(H_2O)_6\right]^{3+} \underset{H+}{\overset{-H+}{\leftrightarrows}} \left[Cr(H_2O)_5\,OH\right] \rightleftharpoons \left[(H_2O)_4\,Cr \left\langle \begin{matrix} OH \\ OH \end{matrix} \right\rangle Cr(H_2O)_4\right]^{4+}$$

<1>

On further addition of base, a precipitate that consists of H - bonded layers of $Cr\,(OH)_3\ (H_2O)_3$, and readily redisolves in acid, is formed. Within a minute or less however, this precipitate begins "aging" to an oligomeric or polymeric structure that is much less soluble[13,14] .

Additionally Cr^{3+} polymerizes, as a result of hydrolysis and associated reactions, with formation at bridged complexes of less certain composition whose existence is indicated by indirect but substantial evidence. Complexes of this type range from dimmers through polymers of colloidal dimensions to precipitated Cr^{3+} hydroxide. Except under special circumstances such reactions are inevitable in neutral and basic solutions and highly probable in slightly acid solutions.

What makes chemistry of Cr^{3+} complexes interesting though intriguing and often torturous for researchers, is the number of steps and mechanisms possible. Some brief explanations are given below:

Aquation:

Chromium salts (chloride, sulfate, nitrate, etc.) are aqua complexes characterized by ions such as $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5Cl]^{2+}$ and $[Cr(H_2O)_4Cl_2]^{+}$. In aqueous solution, the replacement of coordinated groups by water molecules (aquation) is a common reaction:

$$[CrA_5\,X]^{2+} + H_2O \rightarrow [CrA_5\,H_2O]^{3+} + X^- \qquad <2>$$

Where A = Singly coordinated neutral molecule (e.g. H_2O, NH_3)
and X = Singly charged coordinated negative ion (e.g. Cl, CN, CNS)

The extent of aquation depends on several factors including the relative coordinating tendencies of H_2O and X and concentrations of X. Thus, every aqueous solution of Cr^3 is actually, potentially a solution of aqua complexes. Cr^{2+} (whose complexes are labile) catalyzes such reaction, which are usually quite slow otherwise. Electron-transfer reactions between Cr^{2+} and $[Cr(H_2O)_5\,X]^+$, proceeds predominantly through bridged intermediates $\{[\,Cr\text{-}X\text{-}Cr\,]^{4+}\}$. Ligand transfer accompanies electron transfer . In the investigations establishing these conclusions, the reaction conditions have generally been characterized by relatively low $[Cr^{2+}]$ and relatively high $[H^+]$. With relatively high $[Cr^{2+}]$ and relatively low $[H^+]$ another pathway is available[15] with the rate determining reaction being hydroxy bridged complex $[(H_2O)_4\,X\,CrOH\,Cr]^{3+}$

.

However, the role of Cr^{2+} is very important in industrial applications when plating the thick layers of chromium or Cr-Ni and Cr-Ni-Fe alloys from trivalent chromium solutions as an alternative for Cr^{6+} based solutions. Failure to control the transient levels of Cr^{2+} is recognized as the reason for enabling Cr^{3+} based solution to sustain heavy deposition , where thick layers are needed for "hard" chromium solutions with an appreciable deposition rate. Problems are recognized as massive olation catalyzed by a build up of Cr^{2+} in the high pH region in the vicinity of the cathode. Although, the bulk of electrolyte can be about pH =2 the diffusion layer can reach pH = 4. At this pH and with Cr^{2+} catalysis, oligomeric species would be released in to the bulk of the electrolyte where they would build up and reduce the level of active species and hence the deposition rate.

Hydrolysis

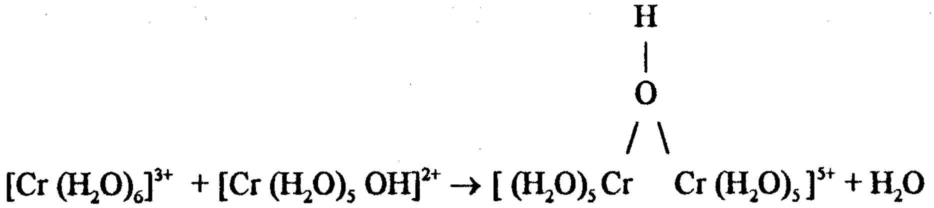
The behavior of aqua complexes as acids leads to, far reaching consequences. The acidity of such solutions is accounted for as follows:

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons Cr(H_2O)_5\ OH]^{2+} + H^+ \qquad <3>$$

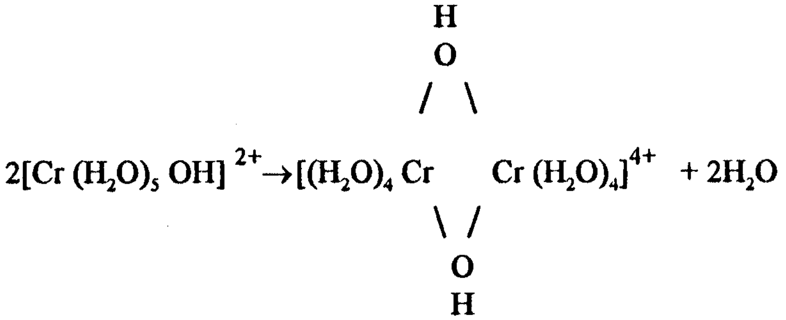
The equilibrium will be displaced to the right by heating and of course, by the addition of base. The order of magnitude of the first hydrolysis constant is $K = 10^{-4}$. As the pH of the Cr^{3+} solution is raised, the equilibrium is shifted and more of the coordinated water molecules may be converted to OH groups which brings in to the picture the new process - olation

Olation

Olated compounds are complexes in which the metal atoms are linked through bridging with OH groups. Such a group is designated as an *ol* group to distinguish it from the hydroxo group i.e., a coordinated OH linked to only one metal atom. The process of formation of ol compounds from hydroxo compounds is called *olation*. Olation results from the formation of polynuclear complexes consisting of chains or rings of Cr^{3+} ions connected by bridging OH groups. The first step of this process may be as follows:



$$[Cr\ (H_2O)_6]^{3+} + [Cr\ (H_2O)_5\ OH]^{2+} \rightarrow [\ (H_2O)_5 Cr \overset{\overset{H}{|}}{\underset{/\ \backslash}{O}} Cr\ (H_2O)_5\ ]^{5+} + H_2O \qquad <4>$$



$$2[Cr\ (H_2O)_5\ OH]^{2+} \rightarrow [(H_2O)_4\ Cr \begin{matrix} H \\ O \\ / \ \backslash \\ \\ \backslash \ / \\ O \\ H \end{matrix} Cr\ (H_2O)_4]^{4+} + 2H_2O \qquad <5>$$

Since the *diol* produced by the reaction 5 is stabilized by the 4-member ring, there is a driving force tending to convert the singly bridged to doubly bridged complex. This diol is produced by polymerization of $[Cr(H_2O)_5OH]^{2+}$, oxidation of Cr^{2+} by molecular oxygen, warming an equimolar mixture of Cr^{3+} and Na OH and boiling an aqueous solution of $[Cr(H_2O)_6]^{3+}$.

The diol and any other polynuclear products containing water molecules (or group that can be displaced by water molecules) can still act as acids, releasing hydrogen ions and leaving coordinated OH groups.

The "Continued process of olation"

Instead of reaching a definite termination, reaction <5> may continue with the formation of larger and larger molecules, the polymers. This may continue if the product of each successive step contains aqua or hydroxo groups. The ultimate consequence is precipitation of chromium hydroxide", $Cr(OH)_3 \bullet X\,H_2O$, a tri-dimensional olated complex.

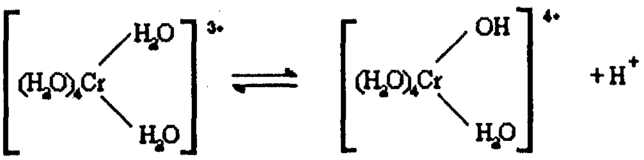
The continued process of olation starts with the hydrolysis of salts of such metals as Al or Cr. The acidity of solution of such salts is due to conversion of aqua to hydroxo groups:

$$[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H^+ \qquad <6>$$

$$[Cr(H_2O)_5]^{2+} \rightleftharpoons [Cr(H_2O)_4OH]^{+} + H^+ \qquad <7>$$

The degree of hydrolysis increases as the temperature is raised and depends on the nature of the anion and especially on the pH of the solution. If alkali is added to warm solution of hydrolyzed chromium salt but not enough for complete neutralization, the polymerization occurs, instead of the precipitation of the basic salt or hydroxide.

This can be explained on the basis of a series of hydrolytic and olation reactions. The first step might be presented as :



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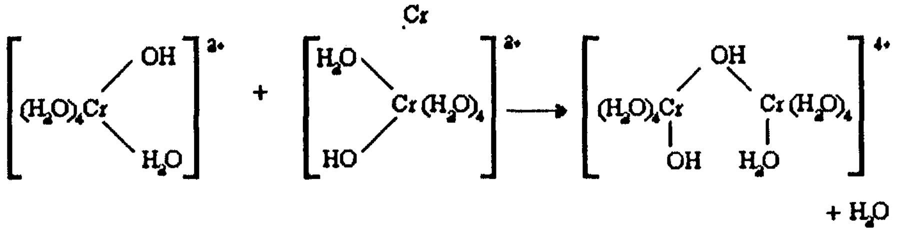

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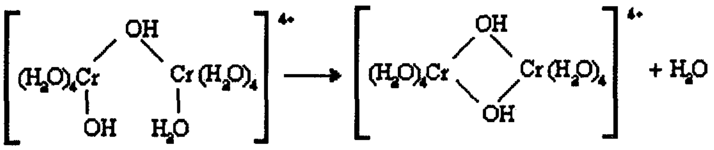
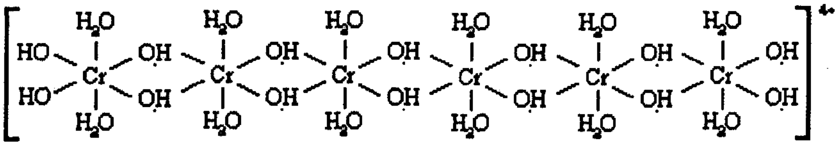
If the reacting groups in each ion are in the cis positions, a completely olated ion may be formed



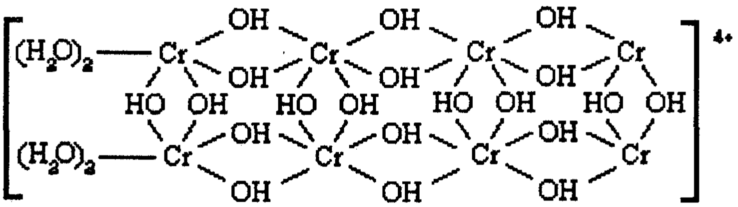
<10>

Further hydrolysis and olation might result in such polymers as the tetrahydroxy-dodecaquo-μ-decaol-hexachromium (III) ion:



<11>

If the agua groups are attached to the metal atoms at the end of the chain, *cross-linked* polymers are formed:



<12>

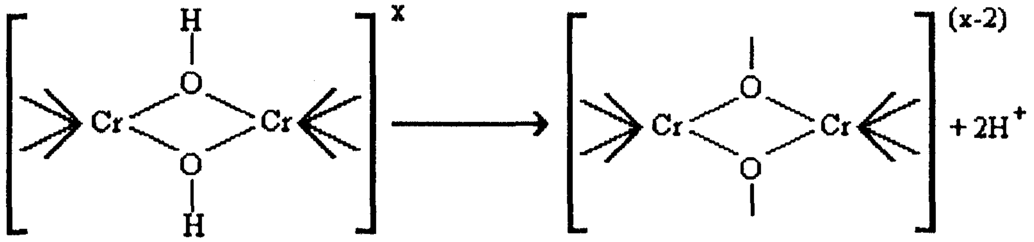
Because of the octahedral configuration of complexes of metals such as chromium, the bonds of a given metal occur in pairs, each of which lies in a plane perpendicular to the planes of the other two pairs. Thus, such cross-linked polymers are three-dimensional.

These processes account for the results obtained when a warm solution of a chromium salt is titrated with a base. With the addition of an increment of base, the pH rises immediately, but falls slowly if the solution is allowed to stand before more base is added. This continues with successive increments of base until enough base has been added to precipitate the hydrated oxide. As base is added to the solution, the hydrogen ions are removed. The equilibrium then shifts in the direction of further hydrolysis and olation, with the formation of more hydrogen atoms. In this way an amount of base can be added without precipitation, which would otherwise cause precipitation if it were added all at once.

The process of olation is favored by an increase in concentration, temperature, and basicity. The process reverses slowly when solution of olated complexes are diluted or when the solution is cooled; i.e., olation decreases the reactivity of coordinated OH groups.

Oxolation

Oxolation may accompany of follow olation, particularly if the reaction mixture is heated. This reaction converts bridging OH^- groups to O^- groups:



<13>

Olation and oxolation may account for changes in reactivity of chromium hydroxide as it ages. Freshly precipitated chromium hydroxide usually dissolves quite rapidly in mineral acids, but after standing some hours it becomes difficult to dissolve. Presumably, olation continues in the precipitate; since bridged OH^- groups react more slowly with acids than singly coordinated OH^- groups the reactivity of the precipitated hydroxide progressively diminishes. If the hydrate is heated, there is a drastic decrease in reactivity due to oxolation, a process even more difficult to reverse than olation. While olation and oxolation are both reversible, the long time required for the acidity of solutions, which have been heated and then cooled, to return to the original value, leads to the conclusion that deoxolation is extremely slow. In general *ol* groups are more readily depolymerized than *oxo* compounds, since protons react more rapidly with *ol* than with *oxo* groups.

Anion penetration

It is well known that the addition of neutral salt to solution of basic sulfate changes the hydrogen ion concentration. Coordinated water molecules, OH^- group, OH^- bridges or other ligands are replaced by anions in the solution. The extent to which anion penetration occurs with *ol* complexes is determined by the relative coordinated tendencies of the entering anions and the groups which it replaces, and the length of time which solutions are allowed to stand[20]. Anions that can enter the coordinated sphere easily and displace OH groups can effectively prevent olation. Penetration by anions into basic chromium complexes decrease in the following order[21]:

oxalate > glycinate > tartarate > citrate > glucolate > acetate > monochloracetate > formate > sulfate > chloride > nitrate > perchlorate.

Thus, if solution of $[Cr\ (H_2O)_6]^{3+}$ is required, the only anion should be weekly coordinated nitrate or perchlorate since those of greater coordinating tendency may displace one or more of the coordinated molecules. In the stock solution of the basic chromium(3+) sulfate, Serphas et al.[20] found ionic species having molecular weights of 68.000.

Reaction rates

After some parameter of a system containing Cr^{3+} complexes is changed, the correspond- ing change in composition of the complexes generally occurs only slowly. Heating a solution (or dispersion) of such complexes promotes olation and oxolation, both of which reverse at a low rate when the system is cooled; reversal of oxolatio much slower than reversal of olation. If the pH of a solution containing olated complexes is reduced to a value at w normally only monometric Cr^3 complexes would exist, it may take a long time for the state of aggregation corresponding to the new pH to be attained.

Complexity of coordination chromium chemistry is presented in figure 1.

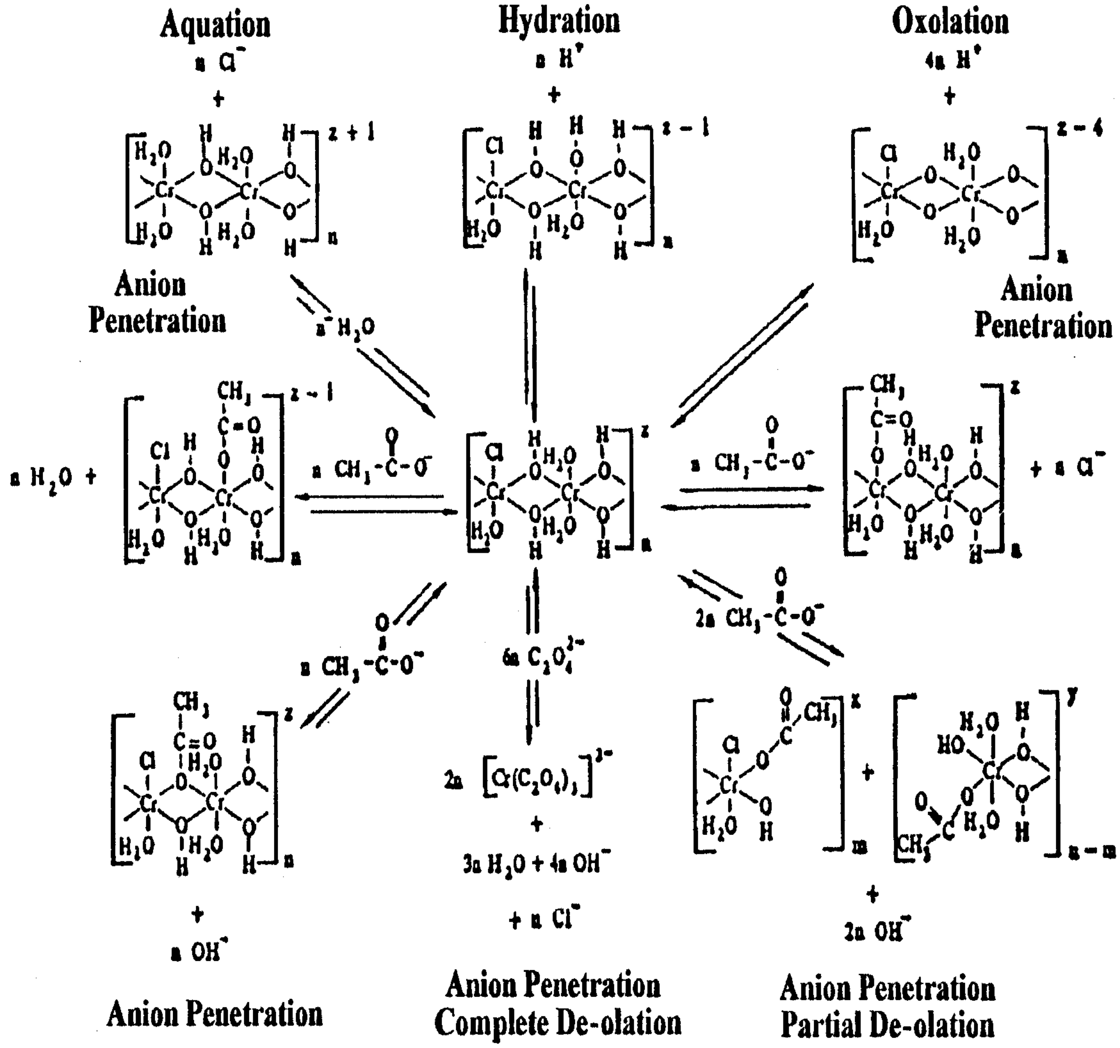


Figure 1. Reactions of Polymeric Olated Cr (III) Complexes.

HEXAVALENT CHROMIUM

The mechanisms of the electroreduction of chromic acid are of great interest, not only from a theoretical point of view, but also for its application in industry. The vast majority of decorative and almost all hard chrome plating are carried out using CrO_3 as the electrolyte. The fact that chromium could be deposited from Cr^{6+} solution, but <u>not</u> from simple aqueous solutions of lower valency salts is unfortunate from the following reasons:

a. Since the electrochemical equivalent of Cr in a CrO_3 solution is 0.3234 g/hr. and cathode current efficiency is 10-20%, one A·hr yields only 0.032 to 0.064 g of metal. This is 15-30 times less than nickel, 18-36 times less than copper from acid solution and 63-126 times less than silver. The only way to offset this is to increase the current density and plating time.

b. The minimum current density at which electrodeposition takes place is two to three orders of magnitude larger than in the case of the other metals (Zn, Ni, Sn, Ag, Au, etc.).

c. The electrodeposition of Chromium is more sensitive to operating conditions (temperature and current density) than any other deposition process.

d. In contrast to other processes, the cathodic current efficiency varies inversely with temperature but is proportional to current density (which causes low throwing power).

e. On the positive side, sixvalent chromium electrolytes are relatively less sensitive to the presence of impurities and the anode material is lead which can easily be made to conform to any shape.

Despite its paramount technological importance and with all the advances of modern science and instrumentation, exact mechanisms of electrodeposition mechanism is still open for conjecture. The main difficulty is the necessary formation and presence of cathodic film on the surface of the metal being plated. The argument, whether the reduction of Cr^{6+} ions to chromium is direct or indirect, during the last decade developed into a discussion of whether the cathode film is useful or not (and how it should be modified to improve the process), since the existence of this film is no longer in question.

This is why it is important to understand the chemistry of chromium with all its intricacies of condensation, polymerization, number of different valent states, ability to make anion/cation compounds (e.g. $Cr_2 (Cr_2 O_7)_3$), existence of a number of double-salts (alumns), isomers, oxidydrates, etc..

Virtually all Cr^{6+} compounds contains a Cr-O unit; the halide CrF_6 is the sole exception. The other Cr^{6+} halides have formula CrO_2X_2, where X= F, Cl, or Br.

The primary Cr-O bounded species is chromium (6+) oxide, CrO_3, which is better known as chromic acid, the commercial and common name. This compound also has aliases chromic trioxide and chromic acid anhydride. Chromium (6+) forms a large number and considerable variety of oxygen compounds most of which may be regarded as derived from Cr^{6+} oxide. These include the oxy-halogencomplexes and chromyl compounds, chromates, dichromates, trichromates, tetrachromates and basic chromates. All this Cr^{6+} compounds are quite potent oxidizing agents, although kinetically they cover a wide range; Cr^{6+} does not appear to have anywhere the capability of forming isopoly anions so characteristic of molybdenum and tungsten.

Chromic trioxide has a molecular weight of 100.01 and forms dark red prismatic crystals which belong to the orthomorphic system, the bypyramidal subclass. Density of the solid is 2.79 g/cm^3. It melts, with some decomposition at 197^0C. CrO_3 is very hydroscopic. Its solubility in water varies from 61.7% at 0^0C. to 67.5% at 100^0C. Oxidation potentials of CrO_3 and chromate solutions are augmented by increasing the acidity of the solution.

Oxidation potentials[23] at 23^0 C are listed in Table 3 and thermodynamic data for some of the chromates at 25^0 C ions are in Table 4.

Reaction	E^0, V
$Cr^{3+} + 4H_2O \rightarrow HCrO_4^- + 7H^+ + 3e^-$	-1.3
$Cr^{2+} + 4H_2O \rightarrow HCrO_4^- + 7H^+ + 4e^-$	-0.9
$Cr^0 + 4H_2O \rightarrow HCrO_4^- + 7H^+ + 6e^-$	-0.4
$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^-$	-1.5
$Cr^{2+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 4e^-$	-1.1
$Cr^0 + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 6e^-$	-0.6
$HCrO_4^- \rightarrow CrO_4^{2-} + H^+$	-0.2

Table 3. Oxidation Potentials for Chromate Ions[25]

Ion	Entropy, Cal/^{0} K/mole	Entrophy of Formation Cal/^{0} K/mole	Heat of Formation Cal/mole	Free energy of Formation Cal/mole
CrO_4^{-2}	10.5 ± 1	−124.5 ± 1.0	−208,500	-171,400
$HCrO_4^{-1}$	-	-	-	-180,140
$Cr_2O_7^{-2}$	-	-	-	-305,800

Table 4 . Thermodynamic Data for Chromate, Chromate and Dichromate Ions .

Chromic Acid $HCrO_4^-$ or $CrO_3 \cdot H_2O$, is not known except in solution. Here it shows a marked tendency to form polyacids by elimination of water.

$2\ H_2CrO_4 \rightarrow H_2O + H_2Cr_2O_7$ (dichromic acid) <14>
$3\ H_2CrO_4 \rightarrow 2H_2O + H_2Cr_3O_{10}$ (trichromic acid) <15>
$4\ H_2CrO_4 \rightarrow 3H_2O + H_2Cr_4O_{13}$ (tetrachromic acid) <16>

The change from H_2CrO_4 to $H_2Cr_2O_7$ is rapid, but the further polymerization takes a measurable time.

The color of CrO_3 indicates that it is itself highly polymerized for it is redder than the di-of trichromates and is approached in color by the tetrachromates.

Depolymerization of $(CrO_3)_\infty$ on solution in water is very rapid. it also seams to depolymerize on heating.

Chromic trioxide can be produced by the action of water on chromyl fluoride. It is most commonly produced, however, by action of concentrated sulfuric acid on a chromate, usually sodium dichromate.

A boiling persulfate solution, in presence of silver ion as catalyst, oxidizes chromic salts to chromic acid, and this method can be used to rejuvenate spent $K_2Cr_2O_7 / H_2SO_4$ laboratory "cleaning" solution [24]

CrO_3 is a powerful oxidizing agent. Bromine has no action on CrO_3 solutions. Iodine, however, turns a solution of CrO_3 black, probably forming chromium hypoiodite. In the presence of sulfuric acid, iodine is oxidized to iodic acid by CrO_3.

Chromates and Dichromates

Chromates are salts of, the hypothetical chromic acid H_2CrO_4. Salts of the hypothetical polybasic chromic acids, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$, $H_2Cr_4O_{13}$, etc., are known as dichromates, trichromates, tetrachromates, etc., respectively. Basic salts, derived from hypothetical para and ortho chromic acids H_4CrO_5 and H_6CrO_6, also exist.

Acid solutions of chromic salts are also oxidized to chromates by permanganates and hydrogen peroxide. In alkaline solution, chromic salts are oxidized by hydrogen peroxide, persulfates, oxides of noble metals, hypochlorites, hypobromites, etc..

Electrolytic oxidation, in either acid or alkaline solutions, will also convert chromic salts to chromates.

The chromate ion and most of the normal solid chromates are yellow, but on acidifing, the solutions pass through orange to red. The dichromates are red in the solid state and in solution. The higher polychromates are even reader than the dichromate in the solid state. Although the various ions, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$, etc., exist together in equilibrium in solution, the ions higher than dichromate probably exist only in the most concentrated solutions. Water is easily added to the higher polychromate ions reverting them to the dichromate. On further dilution, even the dichromate ion adds water forming the reverting them to the dichromate. The $HCrO_4^-$ ion exists in quantity only in dilute solution.[25]

The colors of the salts of chromic acid are interesting. With a few exceptions the monochromates are yellow. The exceptions, already mentioned are dark red to black. The dichromates as already mentioned are orange to red. The trichromates are redder and the tetrachromates still redder. The dark-red color seems to intensify with increasing polymerization. Chromic anhydride, itself in solution, must be highly polymerized. It is approached in intensity of color only by the tetrachromates. Most of the basic salts of chromic acid are yellow. There are exceptions, e.g., the basic lead chromates are scarlet.

In basic solutions above pH = 6, CrO_3 forms the tetrahedral yellow *chromate* ion CrO_4^{2-}; between pH 2 and 6, CrO_4^- and the orange-red *dichromate* ion $Cr_2O_7^{2-}$ are in equilibrium; and at pH values < 1 the main species is H_2CrO_4 . The equilibria are the following:

$$H_2CrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \qquad K = 10^{-5.9} \qquad \Delta F^0 = 8850 \text{ cal.} \tag{<17>}$$

$$H_2CrO_4^- \rightleftharpoons HCrO_4^- + H^+ \qquad K = 4.1 \tag{<18>}$$

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad K = 10^{-2.2} \qquad \Delta F^0 = 2240 \text{ cal.} \tag{<19>}$$

In addition there are the base-hydrolysis equilibria:

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-} \tag{<20>}$$

$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O \tag{<21>}$$

which have been studied kinetically for a variety of bases.

The pH-dependent equilibria are quite labile, and on addition of cation that form insoluble chromates (e.g., Ba^{2+}, Pb^{2+} and Ag^+), the chromates and not the dichromates are precipitated. Furthermore, the species present depend on the acid used, and only for HNO_3 and $HClO_4$ are the equilibria as given. Sulfuric acid a sulfato complex is formed in esencially quantitative conversion:

$$CrO_3(OH)^- + HSO_4^- \rightarrow CrO_3(OSO_3)^{2-} + H_2O \tag{<22>}$$

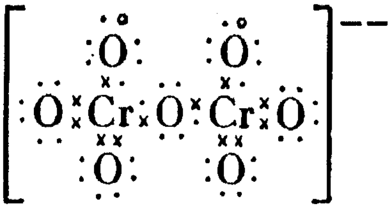


Fig.2. Electronic structure of $Cr_2O_7^{2-}$

Acid solutions of dichromate are strong oxidants:

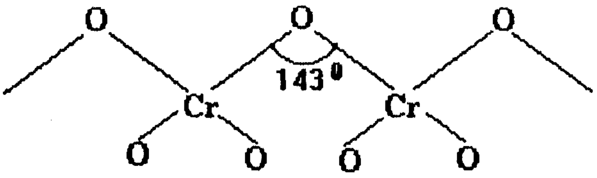
$$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O \qquad E^0 = 1.33\ V \qquad <23>$$

The mechanism of oxidation of Fe^{2+} and other common ions by Cr^{6+} has been studied in detail and with one-and and two-electron reduction respectively, Cr^{5+} and Cr^{4+} are initially formed. The reaction with H_2O_2 in acid solution has a very complex and imperfectly understood mechanism.

The chromate ion in basic solution, however is much less oxidizing:

$$CrO_4^{2-} + 4H_2O + 3e = Cr(OH)_3\ (s) + 5\ OH^- \qquad E^0 = -0.13\ V \qquad <24>$$

The crystalline trioxide $(CrO_3)_\infty$ is built of infinite chains formed by the linking up of CrO_4 tetrahedra:[25]



In which bridging Cr—O bond has the length of 1.75 Å and the C—O and terminal length is 1.6 Å. There are only van der Waals forces between the chains, consistent with the comparatevly low melting point (197° C)

In simple crystalline chromates[27] there are tetrahedral CrO_4^{2-} ions in which is around 1.6 Å, (Fig.3).

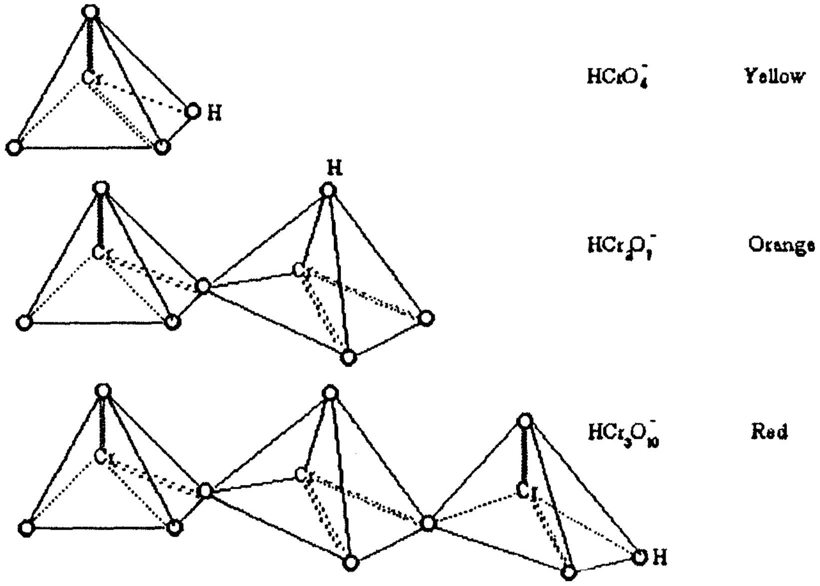
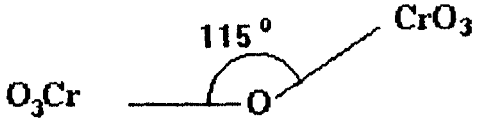


Fig. 3 Chromate Structures.

Polychromates results from sharing corners between CrO_4 tetrahedra. In $(NH_4)_2\ Cr_4O_7$ the anion has the structure shown below:



The central Cr—O bonds were found to be much longer (1·91Å) than the terminal ones (mean 1·6Å.

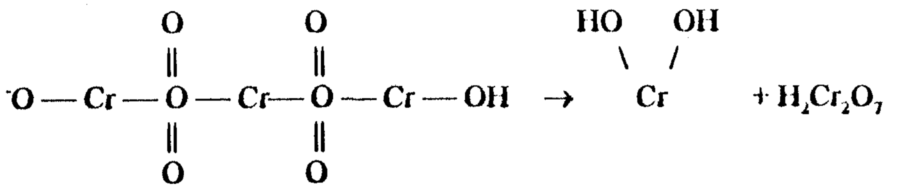
Polychromate ions are of particular interest due to their rule in chromium plating from sixvalent solutions. It is recognized and accepted that chromium cannot be electrodeposited from Cr^{6+} solutions without addition of catalyst usually in form of sulphate. Since the strength of commercial solution is customarily 1-3 Molar, at this concentration, considering the low pH and taking into account the dark red color of the solution, at least tri and possible the tetrachromate are present. It should be noted that in absence of current, the pH of the chromium plating solution is subject to considerable variation, depending on the initial concentration of chromic and sulphuric acids (CrO_3:H_2SO_4= 100:1). If the amount of CrO_3 is increased from 10 to 300 g/l (0.1-3M), the pH changes from 1.4 to 0.08.

Martins and Carpeni with the use of radioactive measured the autodiffusion coefficients of isopolychromates and 25 C in aqueous solution as a function of concentration. Table 4 represents ionic equilibrium dependence on molar concentration. It is evident that in the plating operating ranges ($1.5 < C < 3.5$), the predominant species are di and trichromate ions.

C (mole/l)	Ions in Equilibrium
$C < 10^{-2}$	$HCrO_4^-$
$10^{-2} < C < 10^{-1}$	$HCrO_4 \rightleftharpoons Cr_4O_7^{2-} + H_2O$
$10^{-2} < C < 1,5$	$Cr_4O_7^{2-}$
$1,5 < C < 3,5$	$3Cr_2O_7^{2-} + 2H \rightleftharpoons 2Cr_3O_{10}^{2-} + H_2O$
$3,5 < C < 7,5$	$Cr_3O_{10}^{2-}$
$7,5 < C < 10$	$4Cr_3O_{10}^{2-} + 2H \rightleftharpoons 3Cr_4O_{13}^{2-} + H_2O$

Table 5. Ionic Equillbrium of CrO_3 in Water

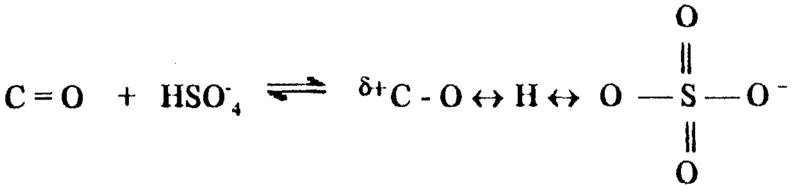
The dominant role of trichomates is advanced by Hoare[27]. According to his phenomenological model, in absence of bisulphate ion (or sulphate - which as this low pH dissociates to bisulphate), trichromate ion in a successive steps (of election transfers and loss of oxygen and reaction with H_3O^+ ion) will decompose to chromons hydroxide going through intermediate step of formation of chromics (3+) and then chromous (2+) dichromates and will finally discharge as cathode as black chromium at very low current efficiency:



$$ {}^-\mathrm{O} - \mathrm{Cr} - \underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{O}}} - \mathrm{Cr} - \underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{O}}} - \mathrm{Cr} - \mathrm{OH} \rightarrow \overset{\overset{\mathrm{HO}\quad \mathrm{OH}}{\backslash\quad /}}{\mathrm{Cr}} + H_2Cr_2O_7 \qquad <25> $$

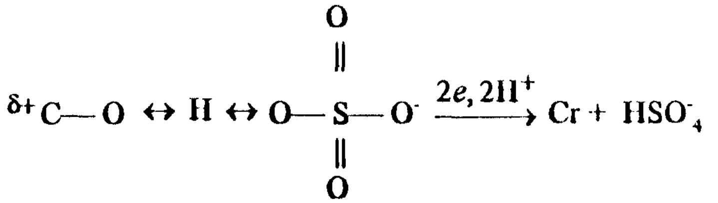
The next step of reduction mechanism is formation of complex between Cr^{2+} hydroxide and bisulphate through hydrogen bonding:

$$ Cr(OH)_2 \rightleftharpoons C = O + H_2O \qquad <26> $$



$$ C = O + HSO_4^- \rightleftharpoons {}^{\delta+}C - O \leftrightarrow H \leftrightarrow O - \underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{S}} - O^- \qquad <27> $$

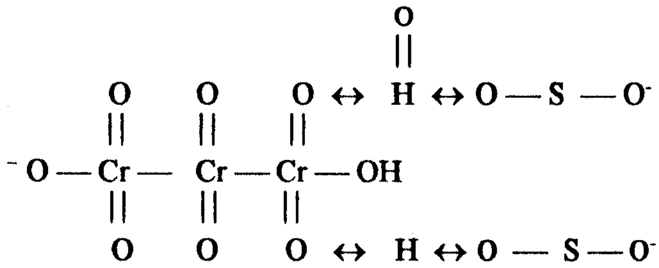
where $\leftrightarrow$ represents the hydrogen bond and $\delta+$ present a dipole generated on chromium end (left side) of the complex. Now, the positively charged complex can be specifically adsorbed on the cathode, two electrons transfered to this end-on configuration with formation of metallic Cr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



$$ {}^{\delta+}C - O \leftrightarrow H \leftrightarrow O - \underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{S}} - O^- \xrightarrow{2e,\, 2H^+} Cr + HSO_4^- \qquad <28> $$

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

The ideally protected trichromate ion would be:



$$\begin{array}{ccccccccccc} & & & & & & & O & & & \\ & & & & & & & \| & & & \\ & O & & O & & O & \leftrightarrow & H & \leftrightarrow O - & S & - O^- \\ & \| & & \| & & \| & & & & & \\ {}^-O - & Cr & - & Cr & - & Cr & - OH & & & & \\ & \| & & \| & & \| & & & & & \\ & O & & O & & O & \leftrightarrow & H & \leftrightarrow O - & S & - O^- \end{array}$$

<29>

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

For fluoride catalyzed CrO_3 based platting systems almost the identical mechanism is proposed[28-a] in which F^- playing a role of blocking agent and catalyst.

Although not complete, this mechanism is most recognized up to this date.

In the recent paper[28], the x-ray diffraction study was carried out in order to identify the predominant species in an industrial CrO_3-H_2O system. Structural analysis shoved that dichromate ions have maximum linehood, but linear-shaped trichromate ions may also exist in significant concentrations. They also concluded that formation of complex <29> can be hardly assumed because of steric hindrance and that is more realistic that *one* HSO_4^- ion acts with polychromate or if heteropoly-acid of type $Cr_2O_6(OSO_3)^{2-}$ is formed.

Very recent paper by Russian workers[29] studied existence of chromium complexes of CrO_3/H_2SO_4 plating solutions for different $X = CrO_3/H_2SO_4$. They concluded that although five different chromium reduces to metal only from this type of complexes

$$[HSO_4]_n^- \cdot [Cr_2O_7]_m^{2-}$$ Where,

$n = 1$; $m = 1$ and $25 < x < 150$ to 200

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

Other recent paper[30] on chromium mechanisms is latest contribution of group headed by Z. A. Soloveva from Institute of Physical Chemistry of Russian Academy of Science. Potentiodynamic and impedance measurements are used to further collaborate their mechanism of deposition based on formation of cathode film (with solid and liquid phase) consisting of oxide-hydroxide Cr^{3+} compounds. A few other Russian groups headed by Professors Schluger, Vargamyan, Levin, N. V. Kudriavtsev, Falicheva, etc., among others contributed a significant amount of research but the problem of final and definite answer is still open.

It is clear at this point that for successful approach and significant further contributions, *in situ* method is needed to study the deposition mechanisms in transients and in steady state conditions.

High pressure from environmentalists is recently stirring up new research in the area of substituting Cr^{6+} solutions to less harmful Cr^{3+}. At the same time, it becomes more and more obvious that mechanisms of deposition from trivalent and six-valent solutions are deeply intertwined and that, in both cases, chromium coordination chemistry is deeply involved.

Research is underway[32] at this moment with the use of *in situ* Surface-enhanced Raman Spectroscopy (SERS) to instantaneously follow cathode film formation, morphology and initial stages of crystallization coupled with valence states identificatioins and distributions in a special cell under construction that combines SERS, ESCA, electron microscopy and polarization measurements simultaneously.

Despite all the research going on on chromium deposition mechanisms in the 1950's, 1960's and 1970's, eventually the flow of the papers on chromium was reduced down to a mere trickle in recent years. The reason is obvious: the complexity of the problem and difficulties involved with highly colored, highly concentrated solutions of chromium salts used, the number of different valent states involved and general lack of in-depth knowledge of chromium coordination chemistry.

What further complicates the matter is that in the beginning (onset) of the deposition process (first 1-3 secs) , one set of reaction 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 $Cr^{6+} \rightarrow Cr^{3+}$ " and this film forms in the first branch of the polarization curve at potentials up to about 700 mv.

Once this film is formed (let's call it from now on C-film, short for compact film), the other cathodic film is formed on the top of C-film and closer to the bulk of the solution: L-film (L-film is short for liquid film).

Significant Japanese contributions toward explination of discussed mechanisms passed (unfortunately) mainly unnoticed due to language barriers. The author of this paper went to considerable labor, pain, and expense to obtain correct translations of some of the Japanese papers. Due to their apparent importance, the final portion of this paper is devoted to them.

Japanese School of Thought on Cr Deposition Mechanisms

Yoshida, Suzuki, Doi and Arai[31] studied the behavior and composition of a cathode film with the help of radioactive traces 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 (but a rather simple) plating cell is constructed with a rapid rinsing station. In essence, steel cathode will be plated for a short period of time and C- and/or L-films will be formedand analized..

Since L-film is liquid and dissolvable in either hot plating solution or hot alkali, by dissolution or simple brushing of the L-film, its formation and influence of deposition of metallic chromium was studied. By forming the C- and L-films with labeled Cr or H_2SO_4 and plating in pure (unlabeled) solution and vice versa, they came to the important conclusions that:

(1) The cathode film is composed of two layers with differient forming properties in terms of thickness and composition. The outer layer, referred to as the L-film, and the inner layer, referred to as the C-film, differ in that the L-film contributes the majority of the cathode film, contains sulfate ions and dissolves easily in the electrolyte and is about 10 times thicker than C film.

(2) The C-film has a thickness of about 5 mg/m^2, contains very few sulfate ions and does not dissolve easily in electrolyte.

(3) The cathode film itself does not reduce to metallic chromium. The metallic chromium 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 Figure 4, or primarily an oxolated version of this compound. Assuming that the cathode film is formed from such chromium complexes, the author feels that the L-film is a compound with lower molecular weight, such as in structures (1) and (2), while the C-film is more like (4), a large complex with a high degree of polymerization.

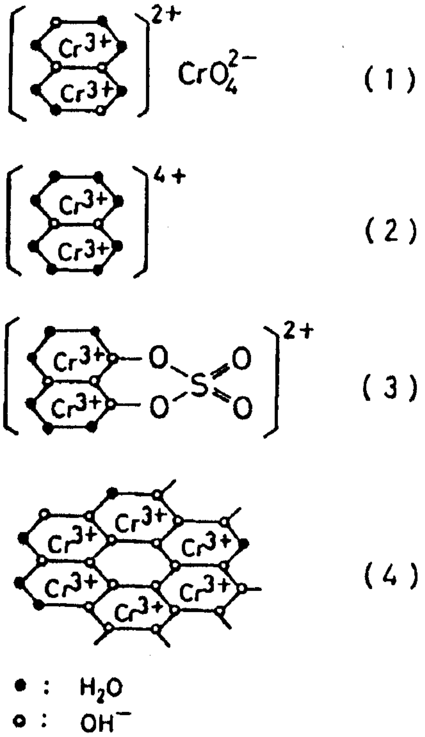


Figure 4 . Chromium Complex Compounds in the Cathode Film.

Nagayma,et al.[33], has assumed that the change from $Cr^{3+} \rightarrow Cr^{2+}$, caused by electroreduction within the cathode film, is a simple one for this type of hydroxy aquo commplex and that some portion of the two-valence chromium obtained in this fashion reacts with Cr^{6+} and is again oxidized to Cr^{3+}, with the remainder being reduced to metallic chromium. Okada[34] holds that SO_4 ions penetrate an olated compound such as that shown in (4) to form a complex such as that in (3), and that from this complex metallic chromium is deposited.

Yoshida, Tsukahara and Koyama[35] used ESCA analysis to further elaborate their previous research[31] where they noted that there are two layers, the L- and C-films, within cathode film. With ESCA analysis, they obtained depth profiling of C- and L-films and demonstrated that C-film is a highly polymerized complex with very few anions present, if any. The L-film appears to be mostly in Cr^{3+} state but the exact valency could not be accurately established, suggesting the possibility of also two- and four-valency.

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

At the end, the whole complicated situation involved around the exact mechanism can be, for the sake of simplicity, described in Figure 4, noting again that this is an oversimplification of one complicated mechanism that happens in different steps electrochemicallyand kinetically and is still poorly understood.

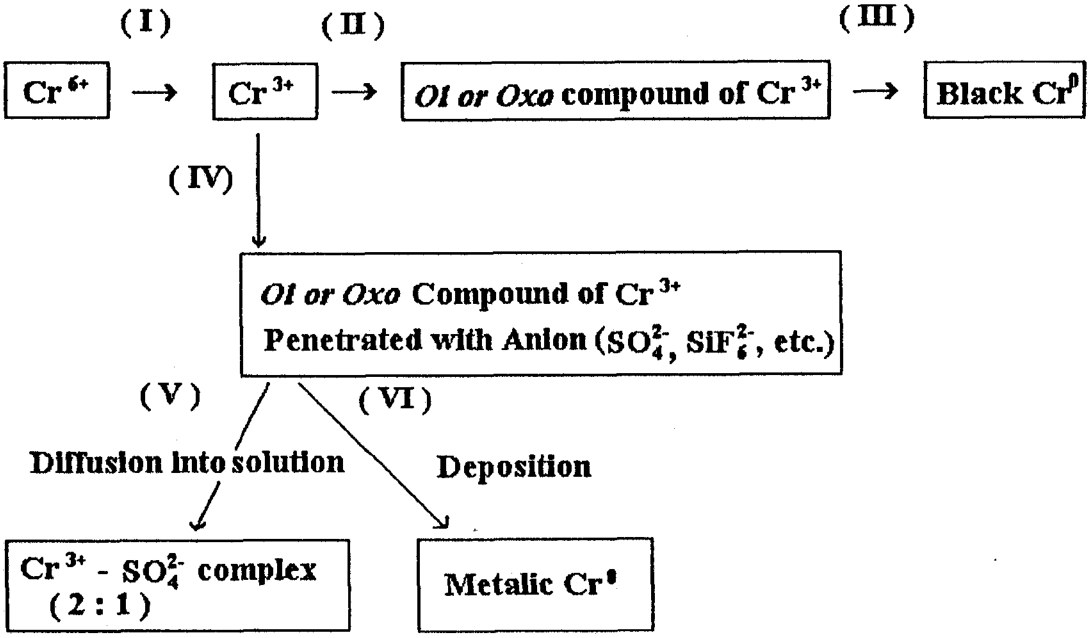


Figure 4. Schematic Representation of the Electrodeposition of Chromium.

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