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Review

Kinetics and Mechanism of Electrochemical Reactions Occurring during the Chromium Electrodeposition from Electrolytes Based on Cr(III) Compounds: A Literature Review

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Abstract: A literature review was conducted to examine the current understanding of the kinetics and mechanism of electrochemical reactions occurring during the electrodeposition of chromium coatings from electrolytes based on trivalent chromium compounds. The research in this scientific field is crucial, as it addresses the pressing need for an alternative to chromium plating processes that rely on solutions containing highly toxic and harmful hexavalent chromium compounds. Numerous literature data on the kinetics and mechanism of the stepwise reduction process of Cr(III) complex ions were analyzed. The influence of various additives and surfactants on the reaction kinetics of the stepwise reduction of trivalent chromium ions was considered. Special attention was given to the kinetics of the stepwise discharge of trivalent chromium ions in ionic liquids and deep eutectic solvents.

Keywords: chromium; trivalent chromium compounds; kinetics; mechanism; electrodeposition

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1. Introduction

Electrodeposition of chromium-based coatings is regarded as a key surface finishing process in modern surface engineering for metal surfaces, owing to the unique properties of chromium coatings and the specific characteristics of chromium compound chemistry and electrochemistry [1–3]. Chromium coatings typically exhibit remarkable resistance to abrasive wear and are widely used for reducing the friction coefficient in contacting surfaces of machinery and mechanisms. The low friction coefficient of chromium-based coatings enables their application in the manufacturing of shafts, piston rings, and similar components. Furthermore, the high microhardness of chromium electrodeposits should be particularly highlighted, as it significantly surpasses that of other electrodeposited metals and alloys.

Despite chromium having a highly negative standard electrode potential ($E^0_{Cr^{3+}/Cr} = -0.74$ V), it passivates in atmospheric conditions due to the formation of a thin, dense, and stable protective oxide layer on its surface. This passivation renders metallic chromium highly resistant to corrosion, particularly in mildly acidic environments. The protective oxide layer not only enhances the corrosion resistance but also prevents interactions with hydrogen sulfide and sulfides, thereby protecting the surface from darkening in polluted industrial atmospheres (a common issue with silver, nickel, and copper coatings). Chromium demonstrates resistance to dissolution in phosphate, nitrate, concentrated sulfate, carbonic acids, aqua regis, and alkaline solutions. Bright chromium deposits are characterized by their high reflectivity, which remains preserved over extended periods of use. This makes them suitable for decorative purposes, reflector manufacturing, and other applications.

Chromium electroplated coatings have been fabricated in industry for many decades from electrolytes based on hexavalent chromium compounds. It should be noted that the process of chromium plating from such electrolytes on an industrial scale was first developed in the 1920s–1930s [4–6].

Electrolytes for chromium plating based on hexavalent chromium contain approximately 100–250 g dm^{-3} of chromium (VI) [1]. It is well known that compounds of chromium in the +6 oxidation state are extremely toxic and harmful to both the environment and personnel [7–9]. Nowadays, due to increased attention to environmental issues, the use of Cr(VI) compounds is strictly limited in the United States, the European Union, Japan, and other industrially developed countries. For example, we can refer to the regulatory acts of the European Union: Directive 2002/95/EC "Restriction of Hazardous Substances" [10] and Directive 2002/96/EC "Waste Electrical and Electronic Equipment," which came into effect on July 1, 2006, and Directive 2000/53/EC "End of Life Vehicle" (fully implemented in July 2007) [11]. In this regard, it should be noted that according to the classification of the International Agency for Research on Cancer (IARC) Cr(VI) compounds are classified as Group 1, representing the highest level of hazard to human health [12]. The toxic, mutagenic, and carcinogenic activity of hexavalent chromium compounds is approximately 500 times higher than that of trivalent chromium compounds [13].

Certainly, the negative effects of using chromium plating electrolytes based on Cr(VI) can be mitigated to some extent by reducing the concentration of chromic anhydride in the solution and optimizing the composition of other electrolyte components and electrolysis conditions [14–20]. However, a definitive solution to the problem of hexavalent chromium in surface electrochemical finishing technologies can only be achieved through the complete elimination of its use. Therefore, the development of chromium plating processes involving the Cr(III) salts as an alternative to environmentally hazardous Cr(VI)-based processes is an extremely important task [21].

It should be noted that systematic research aimed at developing processes and technologies for chromium plating from electrolytes containing trivalent chromium has been conducted for over half a century [22–27]. This review is dedicated to discussing and systematizing the works in this scientific direction. The main kinetics and mechanism of the chromium electroplating process are examined. Special attention is given to the patterns of chromium electroreduction and electrodeposition from ionic liquids and their modern analogs. This review does not cover numerous studies related to the applied aspects of chromium electroplating and electrodeposition of chromium alloys (except for some research on the formation of chromium alloys with metalloids) and composites based on chromium since these topics clearly deserve separate consideration.

2. Kinetics and Mechanism of the Reactions during the Electrodeposition of Coatings from Electrolytes Based on Cr(III)

2.1. Water-Based Electrolytes Containing Salts of Trivalent Chromium

2.1.1. Main Features of Reaction Schemes and Mechanisms

It has long been established that both on a mercury-dropping electrode and on solid electrodes, the electroreduction of Cr(III) ions from aqueous electrolytes proceeds through intermediate stages involving the formation of Cr(II) complex ions [27–32]. For instance, as early as 1929, it was shown [28] that during the electroreduction of Cr(III) ions two distinct current waves are observed on the polarogram, which are well-separated and correspond to the following stepwise discharge reaction scheme:

$$\mathrm{Cr(III)} \xrightarrow[E^0=-0.41\ \mathrm{V}]{+e^-} \mathrm{Cr(II)} \xrightarrow[E^0=-0.91\ \mathrm{V}]{+2e^-} \tag{1}$$

I stage II stage

where E^0 is the standard equilibrium potential of the respective reduction stage (the potential is given with respect to the saturated calomel electrode).

In subsequent studies, the stepwise nature of the discharge reaction of Cr(III) ions with the formation of intermediates, Cr(II) ions, was practically undisputed, although there were isolated works that proposed a one-step mechanism involving the simultaneous transfer of three electrons [33]. However, such a hypothesis is doubtful and has not received any serious justification or support in the further literature. According to the classical theory of charge transfer [34–37], the simultaneous transfer of two electrons requires the activation energy four times higher than the corresponding value for sequential electron transfer. Therefore, in the elementary act of electrochemical interaction, it is most likely that only one electron is transferred. Simultaneous transfer of multiple electrons is theoretically possible if the formation of intermediate compounds during sequential charge transfer is energetically unfavorable. The stabilization of intermediates can occur through their strong adsorption on the electrode surface [38].

Datta [27] investigated the electrochemical reduction of trivalent chromium ions from citrate complexes and demonstrated that this process occurs stepwise with the formation of intermediate Cr(II) ions. It was shown that the formation of citrate complexes of Cr(II) promotes the deposition of satisfactory quality coatings due to the stabilization of Cr(II) particles, which are easily oxidized in the absence of citrate.

Howarth and Pletcher [31] characterized the process of chromium electrodeposition from an aqueous solution containing sulfate and thiocyanate anions under potentiodynamic conditions on a graphite microdisk electrode. It was found that the evolution of gaseous hydrogen occurs simultaneously with the electroreduction of Cr(III) ions to the metal. Consequently, the current efficiency of the metal deposition reaction is significantly less than 100%, which is typical for virtually all chromium plating electrolytes (both hexavalent and trivalent chromium-based). The evolution of hydrogen leads to an increase in pH in the near-electrode layer and the formation of poorly soluble chromium hydroxide compounds, which can be incorporated into the coating and, consequently, deteriorate its properties. It was also shown that chromium deposition occurs only from specific electroactive forms of chromium complexes present in the electrolyte [31].

Song and Chin [39] applied the rotating disk electrode method to investigate the kinetics of the chromium electrodeposition process from an aqueous electrolyte containing ammonium formate and sodium acetate. It was concluded that the process proceeds stepwise. In the first step, the electroreduction of the complex ion Cr(III) to the divalent state takes place:

$$[\mathrm{Cr(H_2O)_5L}]^{2+} + \mathrm{e}^- \rightarrow [\mathrm{Cr(H_2O)_5L}]^{+} \tag{2}$$

where L stands for a ligand (formate or acetate ion).

This step is followed by the reduction of divalent chromium ions to the metallic state (Cr(m)):

$$[\mathrm{Cr(H_2O)_5L}]^{+} + 2\mathrm{e}^- \rightarrow \mathrm{Cr(m)} + 5\mathrm{H_2O} + \mathrm{L}^- \tag{3}$$

It has been shown that the overall rate of chromium deposition is controlled by the diffusion of trivalent chromium ions in the form of a complex $[\mathrm{Cr(H_2O)_5L}]^{2+}$ towards the cathode surface.

Zeng et al. [40], in their investigation of the kinetics and mechanism of chromium electroplating from a formate-based aqueous solution, focused on determining the composition and structure of Cr(III) complexes. They employed ultraviolet spectroscopy and X-ray photoelectron spectroscopy methods for this purpose. It was shown that trivalent chromium ions are present in the solution in the form of octahedral complexes $[\mathrm{Cr(H_2O)_6}]^{3+}$. According to the authors, this complex structure is unfavorable for the reactivity of Cr(III) ions during electrochemical reduction. In the presence of formic acid, a rearrangement of complexes occurs, leading to the formation of $[\mathrm{Cr(H_2O)_4CHOO}]^{2+}$ ions, which exhibit distorted octahedral geometry with the Cr^{3+} ion at the apex. According to the authors' claim, this particular state promotes the faster discharge of Cr^{3+} ions.

These ideas are consistent with the results of a series of little-known but in-depth studies conducted using quantum chemical modeling [41,42]. According to the obtained data, the transfer of the first electron (i.e., the one-electron reduction of Cr(III) to Cr(II)) does not require significant reorganization of the internal coordination sphere of chromium ions.

In the course of the electrochemical process, only a slight increase in the distances between the central atom and the donor oxygen of the ligand (formate anion) is observed, resulting from a change in the hybridization of valence orbitals from d^2sp^3 (in Cr^{3+}) to sp^3d^2 (in Cr^{2+}). On the other hand, the electron transfer to Cr^{2+} ions exhibits a fundamentally different energetic behavior. The calculated activation energy for the reaction $Cr^{2+} + e^- \rightarrow Cr^+$ in the case of octahedral complexes is extremely high, making such a transition highly improbable. It has been shown that the attachment of an electron to Cr^{2+} becomes possible only when a significant restructuring of the geometry of the Cr^{2+} complex occurs, resulting in a reacting particle with a biligand complex of linear structure. It has been established, in accordance with the results of quantum chemical calculations, that the discharge of hydroxocomplexes $[Cr^{2+}(OH^-)(HCOO^-)]$ is energetically more favorable [41].

In addition, Seredyuk and Vargalyuk [42] have found that the previously described electrocatalytic action of fluoride ions towards the discharge of Cr(II) is attributed to their incorporation into the inner sphere of the complex, which reduces the positive charge on the central atom, accelerates ligand exchange, and reduces energy consumption during the transition from the electrochemically less-active intermediate $[Cr^{2+}L_6]$ to the electroactive form $[Cr^{2+}L_2]$ (where L represents a fluoride ion). According to the results of quantum chemical calculations, the discharge of linear biligand complexes $[Cr^{2+}L_2]$ requires significantly lower activation energy compared to the discharge of $[Cr^{2+}L_6]$.

The kinetics and mechanism of chromium electrodeposition from electrolytes based on Cr(III) containing two ligands, denoted as K1 and K2, were studied in detail [43]. Based on subsequent studies by these authors, it can be assumed that these ligands correspond to urea and sodium formate, respectively. It was found that the reaction proceeds stepwise, with Cr(II) compounds participating only as intermediate products in the near-electrode layer. According to the authors' findings, the rate of chromium electrodeposition is determined by the chemical reorganization of Cr(II) complexes in the near-electrode layer of the electrolyte, which is the rate-determining step. During the initial step of the process, the complex of trivalent chromium is adsorbed onto the electrode surface:

$$\left[Cr^{3+}(H_2O)_5K2\right]K1 \Leftrightarrow \left[Cr^{3+}(H_2O)_5K2\right]_S + K1. \tag{4}$$

Subsequently, the adsorbed complex undergoes the attachment of the first electron:

$$\left[Cr^{3+}(H_2O)_5K2\right]_S + e \Leftrightarrow \left[Cr^{2+}(H_2O)_5K2\right]_S. \tag{5}$$

In the next step, either deprotonation or replacement of the water molecule by the OH^- ion in the inner coordination sphere of Cr^{3+} occurs (Equations (6) and (7)).

$$\left[Cr^{2+}(H_2O)_5K2\right]_S \rightarrow \left[Cr^{2+}(H_2O)_4(OH)K2\right]_S + H^+, \tag{6}$$

or

$$\left[Cr^{2+}(H_2O)_5K2\right]_S + OH^- \rightarrow \left[Cr^{2+}(H_2O)_4(OH)K2\right]_S + H_2O. \tag{7}$$

After the rate-determining step, the process proceeds as follows:

$$\left[Cr^{2+}(H_2O)_4(OH)K2\right]_S + e \Leftrightarrow [Cr^+(H_2O)_4(OH)K2]_S, \tag{8}$$

$$[Cr^+(H_2O)_4(OH)K2]_S + e \Leftrightarrow \left[Cr^0(H_2O)_4(OH)K2\right]_S, \tag{9}$$

$$\left[Cr^0(H_2O)_4(OH)K2\right]_S \Leftrightarrow Cr^0_{met} + 4H_2O + OH^- + K2. \tag{10}$$

The influence of hydrodynamic conditions on the kinetics of the stepwise discharge of Cr(III) ions has been investigated [44]. The presence of diffusion limitations in the kinetics of the partial discharge of trivalent chromium ions (to Cr(II)) and hydrogen evolution has been established. The process of complete discharge (i.e., electrodeposition) occurs under conditions of mixed kinetics.

The kinetics and mechanism of the stepwise chromium electrodeposition process from formate, oxalate, and aminoacetate electrolytes based on Cr(III) have been revealed in a series of studies [45–50]. Experimental results show that due to a significant difference in the standard potentials of $E^0_{\mathrm{Cr(III)/Cr(II)}}$ and $E^0_{\mathrm{Cr(II)/Cr(0)}}$ electrochemical couples, the discharge of Cr(II) ions starts at potentials where the current density of the Cr(III) electroreduction reaction approaches the diffusion-limiting current density (Figure 1). A certain fraction of Cr(II) ions can diffuse into the bulk electrolyte with a certain rate (ν), and then the following equation is valid:

$$\frac{j_2}{F} = \frac{j_1}{2F} + \nu, \tag{11}$$

where j_2 and j_1 are the partial current densities of the electroreduction reactions of Cr(III) to Cr(II) and Cr(II) to Cr(0), respectively.

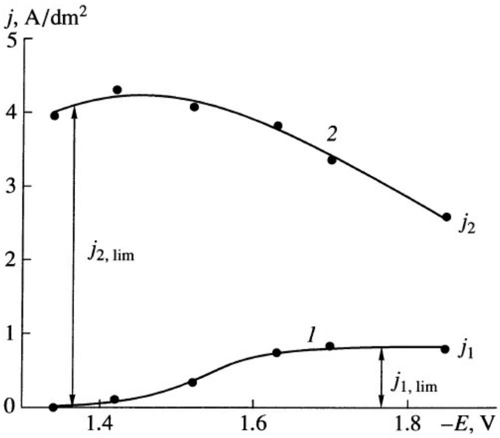

Figure 1. Partial polarization curves associated with the electrodeposition reaction Cr(II) → Cr(0) (1) and electroreduction reaction Cr(III) → Cr(II) (2). Chromium electrolyte contained (mold m^{-3}): 0.5 $KCr(SO_4)_2$, 1.0 aminoacetic acid, 2.0 ammonium sulfate, and 0.5 boric acid; pH 2.0; temperature 298 K. Reproduced from [46] with permission from Springer Nature.

For the entire investigated potential range, the inequality $j_1 < 2j_2$ holds, which means that $\nu > 0$. This indicates that the process of chromium deposition involves partial diffusion of intermediates (Cr(II) ions) from the electrode surface into the bulk solution. Figure 2 illustrates the distribution of current densities between electrode reactions during chromium electrodeposition [46].

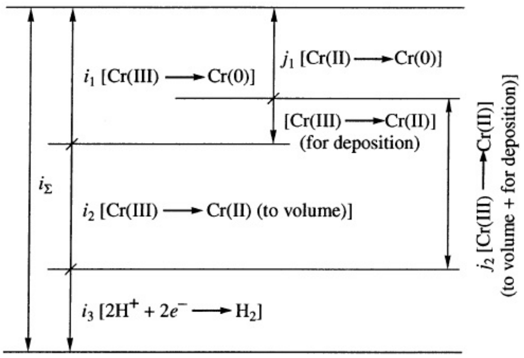

Figure 2. Scheme showing the current density distribution between electrode reactions during chromium electrodeposition. Reproduced from [46] with permission from Springer Nature.

Chromium electrodeposition from aqueous electrolytes is accompanied by the concurrent reaction of hydrogen evolution (Figure 2). The occurrence of this reaction becomes possible because chromium is a sufficiently electronegative metal and the discharge of chromium ions occurs at very negative electrode potentials (Figure 1). The hydrogen evolution reaction implies an increase in pH near the electrode surface. As a result of a local increase in pH in the near-electrode layer, the formation of chromium (III) hydroxide and a number of chromium hydroxo-complexes is possible [39,43,44,46–50]. As follows from the Pourbaix diagram (potential vs. pH diagram) for chromium compounds [51], Cr(III)-containing species can exist as Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3$ (aq), and $Cr(OH)_4^{-}$, depending on pH value (Figure 3). Thus, $Cr(OH)_3$ (aq) predominates at pH $\approx$ 6–11, while hydroxo-complexes of Cr(III) start to form at pH > 3. Such conditions can actually arise in the near-electrode layer during chromium electrodeposition, which is accompanied by intense hydrogen evolution and a corresponding local decrease in electrolyte acidity. A colloidal near-surface film containing chromium (III) hydroxide strongly affects the kinetics of electrodeposition and the properties of the resulting coatings [45–49]. The formation of hydroxo-complexes of divalent and trivalent chromium ions is taken into account in almost all reaction schemes and mechanisms of chromium electrodeposition described in the literature.

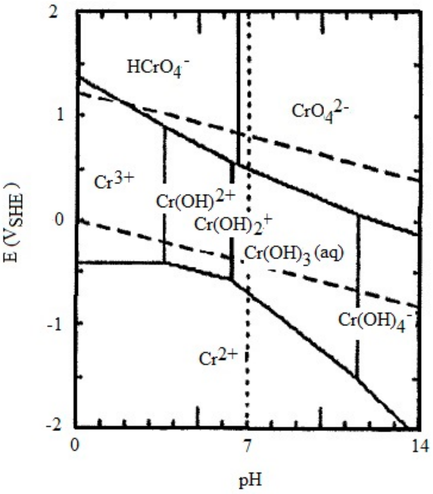

Figure 3. Pourbaix diagram for dissolved chromium species at 25 °C. Reprinted from [51], Copyright 1997, with permission from Elsevier.

An increase in the concentration of formic, aminoacetate, or oxalic acid leads to a certain inhibition of the metal electrodeposition process (a shift of the exponential region of the j_2 vs. the E curve towards more negative potentials). With increasing pH in formate and aminoacetate electrolytes, the rate of chromium electrodeposition increases, while in oxalate electrolytes, it decreases. These observations suggest that the process mechanism is complicated by certain chemical stages. Therefore, in deriving the equations for the polarization curve, it was taken into account that the Cr(II) ion discharge may be preceded by a fast chemical reaction in which the electroactive form of the $Cr(II)_{EAC}$ complex is formed:

$$\mathrm{Cr(II)_{init}} + \sum_{i} \nu_i X_i \rightleftarrows \mathrm{Cr(II)_{EAC}} + \sum_{j} \nu_j X_j, \tag{12}$$

where $\mathrm{Cr(II)_{init}}$ represents the products of the preceding incomplete electrochemical reduction reaction of Cr(III) complex ions, and $X_{i\ (j)}$ represents possible participants in the reaction leading to the formation of electroactive forms of the complexes (such as H^+ ions, OH^- ions, solvent molecules, organic ligands, etc.).

Mathematical models have been developed that adequately describe the kinetics of stepwise electrodeposition of chromium both on a stationary electrode and a rotating disk electrode [46,47]. Reaction schemes for the chromium electrodeposition processes from Cr(III) salt solutions have been proposed. For example, in formate and aminoacetate electrolytes the electroactive forms of the complex are hydroxo-complexes of Cr(II), which are formed on the electrode surface as a result of the dissociation of internally coordinated water molecules:

$$\begin{aligned}[\mathrm{Cr(II)(HCOO)}_{\mathrm{m}}(\mathrm{H_2O})_{\mathrm{n}}]_{\mathrm{ads}}^{(2-\mathrm{m})} \Leftrightarrow {} & [\mathrm{Cr(II)(HCOO)}_{\mathrm{m-k}}(\mathrm{H_2O})_{\mathrm{n-1}}(\mathrm{OH})]_{\mathrm{ads}}^{(1-\mathrm{m+k})} \\ & +\mathrm{kHCOO}^- + \mathrm{H}^+, \end{aligned} \tag{13}$$

$$\begin{aligned}&[\mathrm{Cr(II)(HCOO)}_{\mathrm{m-k}}(\mathrm{H_2O})_{\mathrm{n-1}}(\mathrm{OH})]_{\mathrm{ads}}^{(1-\mathrm{m+k})} + 2\mathrm{e}^- \\ &\rightarrow \mathrm{Cr}^0 + (\mathrm{m}-\mathrm{k})\mathrm{HCOO}^- + (\mathrm{n}-1)\mathrm{H_2O} + \mathrm{OH}^-, \end{aligned} \tag{14}$$

where m = 1, 2; k = 0, 1, 2; n = 1, 2, ...

During the electrodeposition of metal from an oxalate electrolyte, the electroactive species can be the corresponding oxalate chromium complexes. The direct reduction of these complexes at the cathode leads to the formation of the metallic deposit:

$$[\mathrm{Cr(II)(HC_2O_4)(H_2O)}_{\mathrm{n}}]_{\mathrm{ads}} + \mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{Cr}^0 + \mathrm{H_2C_2O_4} + \mathrm{nH_2O}. \tag{15}$$

However, the partial polarization curves of chromium deposition often exhibit current wave-like patterns with peaks that cannot be directly explained by the proposed kinetic equations. An analysis of the literature and experimental data has led to the conclusion that these peaks are associated with the formation of low-solubility hydroxide phases of Cr(III) in the near-electrode layer, which can partially block the electrode surface [46,47,49].

Protsenko et al. [48] utilized the theory of similarity and dimensional analysis for the interpretation of the results obtained from investigating the kinetics of the stepwise process of chromium electrodeposition from electrolytes based on Cr(III) salts. A corresponding universal system of dimensionless complexes has been developed. The theory of similarity and dimensional analysis is a powerful analytical tool, the potential of which is still underutilized in electrochemical science [52–55]. The physical interpretation of each dimensionless complex (similarity criterion) was analyzed, and the dimensional relationships derived from the experimental data were discussed [48].

It should be noted that the mechanisms of electrode processes proposed in the series of studies [46–50] have been subsequently used with minimal modifications in the works of several other authors [56–60].

2.1.2. Main Influencing Factors and Some Results Published in the Last Few Years

One of the classical methods to influence the kinetics of electrochemical metal deposition reactions is the use of surfactant additives [61]. The electrodeposition of chromium from solutions of its trivalent compounds is accompanied by the formation of various phases in the near-electrode region such as an electrolyte, colloidal particles of sparingly soluble chromium hydroxides, a metal, and hydrogen bubbles. The colloid-chemical properties of these phase boundaries significantly affect the kinetics of electrochemical processes and, consequently, the properties of the formed deposits. Organic additives introduced into chromium plating electrolytes can act as "conventional" surfactants, specifically adsorbing at certain phase boundaries, in addition to participating in the formation of complex compounds with chromium ions, which strongly affects the mechanism and kinetics of charge and mass transfer.

The kinetics and mechanism of the electroreduction reaction of Cr(III) ions to Cr(II) from perchlorate solutions containing various amino acids, including glycine, alanine, leucine, tryptophan, serine, threonine, phenylalanine, anthranilic acid, aspartic acid, and glutamic acid, were investigated using the method of oscillographic polarography on a mercury electrode [62,63]. The electrochemical parameters of Cr(III) reduction were compared with the spectral characteristics of the corresponding complexes. It was shown that the formation of complexes with amino acids leads to an increase in the polarization of the studied process. The electrochemical reduction of amino acid complexes of Cr(III) occurs irreversibly and is not complicated by stages of amino acid molecule adsorption on the mercury electrode. In this process, complex ions of Cr(III) are directly discharged at the cathode. It was found that, in addition to the thermodynamic stability of Cr(III) complexes, an important factor determining the polarization and irreversibility of the electrode process is the change in the electronic structure of the Cr(III) complex ion. With a decrease in the splitting parameter of the d-orbitals of the Cr(III) ion in the series of its complexes with amino acids, the affinity of Cr(III) for an electron decreases, and accordingly, the electroreduction is slowed down.

Surviliene et al. [64] investigated the influence of formic acid and urea on the kinetics of the electrodeposition process of chromium from a sulfate electrolyte and on the properties of the coatings. It was demonstrated that an "active complex" of the following composition $[Cr(carbamid)_n(H_2O)_{6-n}]^{3+}$ is formed in the electrolyte, where "carbamide" is the product of the condensation of urea and formic acid molecules. The formation of such a complex contributes to the stabilization of kinetic characteristics and electroplating parameters. The effect of hydrazine and hydroxylammonium phosphate additives on the electrodeposition of chromium from a sulfate–formate electrolyte with the addition of "carbamide" was revealed in the study [65]. The obtained data allowed for the consideration that these additives influence the activity of the $[Cr(carbamid)_n(H_2O)_{6-n}]^{3+}$ complex, promoting the stability of the electrolyte functioning.

The adsorption of organic substances on the particles of chromium (III) hydroxide, which is formed in the near-electrode layer, significantly affects the chromium electrodeposition reaction [66]. The adsorption of surfactants leads to the formation of hydroxide sol with optimal dispersion, which improves the appearance of the deposits but has practically no effect on the rate of the electrochemical deposition reaction. At the same time, the use of surfactants capable of specific adsorption on the surface of metallic chromium reduces the current efficiency without deteriorating the appearance of the coatings.

Not only organic surfactants but also water-soluble synthetic polymers can serve as effective regulators of the dispersion of colloidal systems formed in the near-electrode layer during chromium deposition. The influence of polyhexamethylene guanidine and polyvinylpyrrolidone on the electrodeposition of chromium from formate–sulfate electrolyte based on Cr(III) has been investigated [67,68]. The addition of polyhexamethylene guanidine to the electrolyte results in a decrease in the partial rates of the electrochemical processes of Cr(III) to Cr(II) and Cr(II) to Cr(0) electrochemical reduction [67]. It has been shown that this additive forms an adsorption layer on the electrode surface, which hinders charge transfer processes and prevents the incorporation of coarse-dispersed particles of chromium (III) hydroxide into the coating structure. It was found [68] that the addition of polyvinylpyrrolidone acts as a flocculant, reducing the concentration of fine-dispersed particles in the near-electrode layer, thereby preventing their inclusion in the coating and deteriorating its properties.

It has been found that the use of polyethylene glycol as an additive in sulfate–formate chromium-plating electrolyte selectively inhibits the hydrogen evolution reaction, which significantly affects the formation of specific intermediates in the near-electrode layer and alters the morphology and properties of the formed coatings [56,57,69]. According to Zhang et al. [70], the adsorption of methoxy polyethylene glycol additive on the electrode surface leads to the inhibition of both stages of the stepwise electrodeposition of trivalent chromium ions and the hydrogen evolution, which positively influences the physicochemical characteristics of the resulting coatings.

Stepwise reduction of Cr(III) ions during chromium electrodeposition is always accompanied by the occurrence of various electrochemical and physicochemical reactions and processes on the electrode and in the vicinity of the electrode. Among them, one of the most interesting and specific to chromium plating is the codeposition of metalloids (such as carbon, phosphorus, sulfur, etc.).

The codeposition of chromium with phosphorus has been described in a number of publications [71–74]. It has been found that phosphorus in these coatings is present in the form of phosphide. Zeng et al. [73] proposed the following reaction scheme for the formation of Cr–P electroplating:

$$H^+ + e^- \rightarrow H, \tag{16}$$

$$H_3PO_2 + H \rightarrow P + 2H_2O, \tag{17}$$

$$Cr(H_2O)_6^{3+} + 3P + 3e^- \rightarrow CrP_3 + 6H_2O. \tag{18}$$

Thus, the electrochemical reduction of phosphorus occurs during the simultaneous electrodeposition of chromium, and the metal surface serves as a catalyst for this process. In the cited studies, sodium hypophosphite dissolved in the electrolyte was used as a source of phosphorus. However, it is not the only possible source of phosphorus. It has been demonstrated that phosphorus can also co-deposit with chromium during the electroreduction of H_3PO_3 [75].

It is well known that coatings incorporating varying amounts of carbon are formed from chromium plating electrolytes based on Cr(III) containing certain organic components (formate, oxalate, etc.) [2,76–83]. It has been noted that carbon in such electrochemical deposits is present in the form of chromium carbides [77]. It has been repeatedly observed that during the electrodeposition of chromium alloys with metalloids (phosphorus, carbon, etc.), in addition to the stepwise discharge of metal ions and hydrogen evolution, processes of electroreduction of the ligand environment of chromium ions occur at the cathode, leading to the incorporation of metalloids into the electrodeposit [84–86]. Here, enhanced electrocatalytic activity of the juvenile chromium surface plays an important role.

The mechanism of electrochemical deposition of chromium–carbon alloy from formate–urea electrolyte based on Cr(III) compounds has been proposed in the following works [50,87]. According to this mechanism, a certain portion of freshly deposited chromium (active ad-atoms of the metal formed as a result of the discharge of intermediates in accordance with the stepwise mechanism) interacts with adsorbed organic molecules, forming carbon through a particular "chemical" mechanism [87]:

$$2Cr^0_{ad} + C(IV) \rightarrow 2Cr(II) + C(0). \tag{19}$$

The formed carbon is incorporated into the coating, leading to the formation of chromium carbide, while the Cr(II) ions (products of the reaction (19)) can participate again in the reduction process to the metallic state. Importantly, the presence of carbon on the surface of the coating hinders the process of surface diffusion of chromium ad-atoms and, thereby, promotes the formation of a nanocrystalline structure [87]. The incorporation of carbon and the presence of chromium carbide in the coating have significant effects on its properties. The presence of carbide compounds can enhance the hardness, wear resistance, and corrosion resistance of the coating. Additionally, the nanocrystalline structure resulting from the presence of carbon can improve the mechanical properties, such as strength and toughness, of the chromium electrodeposit. Therefore, the formation of chromium–carbon alloy coatings through the proposed mechanism provides a way to tailor the properties of the coatings for specific applications.

Next, let us focus on discussing the results of some studies that directly address the kinetics and mechanism of chromium deposition from Cr(III)-based aqueous electrolytes, which have been published in the last few years.

Wijenberg et al. [60] investigated the influence of current density and hydrodynamic conditions on the mechanism of chromium deposition from a sulfate–formate electrolyte based on Cr(III). They emphasized the significant role of stepwise deprotonation of trivalent chromium complexes, induced by an increase in surface pH due to the hydrogen evolution reaction, the rate of which can be controlled by varying the current density. At relatively low current densities, predominantly well-soluble complexes $[Cr(HCOO)(OH)(H_2O)_4]^+$

exist in the near-electrode layer, and no electrodeposition occurs. In the intermediate current density range, complexes $Cr(HCOO)(OH)_2(H_2O)_3$ are deposited on the surface and a certain portion of them is further reduced to the metallic state, while formate participates in subsequent chemical transformations, acting as a carbon source for the formation of chromium carbide. Finally, at sufficiently high current densities, predominantly $[Cr(HCOO)(OH)_3(H_2O)_2]^-$ complexes are formed in the near-electrode layer, which ultimately leads to the deposition of chromium oxides rather than metallic chromium on the surface. Figure 4 illustrates the corresponding experimental data regarding the dependence of deposited chromium weight on current density at a constant rotational speed. It should be noted that the concept developed by Wijenberg et al. [60] is consistent with the reaction mechanism proposed in previous studies [46–49], which emphasize the important role of the formation of various hydroxo-species and hydroxo-complexes on the near-electrode layer during chromium electrodeposition.

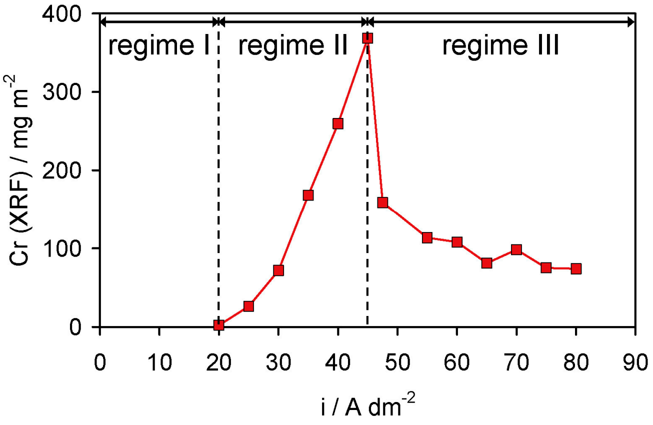

Figure 4. Dependence of deposited chromium weight on current density at a constant rotational speed. Reprinted from [60] Copyright 2015, with permission from Elsevier.

Song et al. [88] conducted an interesting study on the effect of bis-3-sulfopropyl-disulfide on the electrodeposition from a sulfate-based trivalent chromium electrolyte. It was found that this additive accelerates chromium deposition and increases current efficiency. Based on UV-vis spectroscopy and density functional theory modeling, it was hypothesized that, in this case, bis-3-sulfopropyl-disulfide interacts with trivalent chromium, replacing one water molecule in the inert complex $[Cr(H_2O)_6]^{3+}$ to form the complex $[Cr(H_2O)_5(C_6H_{13}O_6S_4)]^{2+}$, in which the bond length between the chromium (III) ion and water molecules is increased. According to the researchers, this enhances the reduction reaction of chromium ions to the metallic state, thereby promoting faster electrodeposition.

Numerous data from the literature suggest that the rate of individual steps of the reduction of trivalent chromium ions and, ultimately, the quality of the obtained chromium deposits, significantly depend on complex formation and speciation in Cr(III) salt solutions. Therefore, serious research is currently being conducted on this issue, including in the context of chromium electrodeposition. In particular, Büker et al. [89] investigated the interaction between Cr(III) ions and certain carboxylic acids (malonic acid, malic acid, oxalic acid, and glycolic acid), which are often used for preparing chromium plating electrolytes. It was shown that the larger the molecule of the carboxylic acid, the slower the reaction of its interaction with trivalent chromium proceeds. The conclusion was drawn about the need for careful control of a specific molar ratio between chromium ions and carboxylic acid molecules, which ensures the optimal rate of the steps of the Cr(III) ion reduction reaction.

Xu et al. [90] investigated the processes of electrochemical deposition of chromium from an electrolyte containing the so-called "ternary complexing agent," a mixture of oxalic acid, tartaric acid, and urea. This work emphasized the crucial role played by the nature and structure of intermediates, namely, the divalent chromium ions, in the multistep reduction of Cr(III). It was found that in the electrolyte of the studied composition, divalent chromium ions form complex ions with dsp^3 and dsp^2 hybridization, which exhibit an enhanced electron affinity and, therefore, facilitate the accelerated reduction reaction to the metallic state. Additionally, the planar geometry resulting from dsp^2 hybridization hinders the formation of hydroxo-bridged complexes due to steric effects. According to Figure 5, the electroreduction of the divalent chromium complexes to metallic chromium occurs via two reaction routes. The first route involves the direct reduction of highly electrochemically active $[Cr(LH)(H_2O)_5]_n$ complexes, while the second route involves the indirect reduction of the less electrochemically active $[Cr(L)(H_2O)_5]_{(n-1)}$ and $[Cr(L\text{–}H)\text{–}(H_2O)_4OH]_{(n-1)}$ species. In a conventional chromium electrolyte containing formic acid (Figure 5a), the generation and accumulation of Cr(II) hydroxo-complexes is observed during electrodeposition (route 2). This results in the formation of inert polymeric species as products of olation processes. Consequently, these adsorbed polymers block the surface, impeding the diffusion of complex ions and decelerating the electrochemical reduction of reactive Cr(II) ions (the first route). As a consequence, the current efficiency decreases and the coating thickness exhibits minimal increase. On the contrary, when the plating electrolyte contains the ternary complexing agent (Figure 5b), the unfavorable olation processes are significantly reduced, allowing for accelerated diffusion of Cr complexes to the electrode surface (the second route).

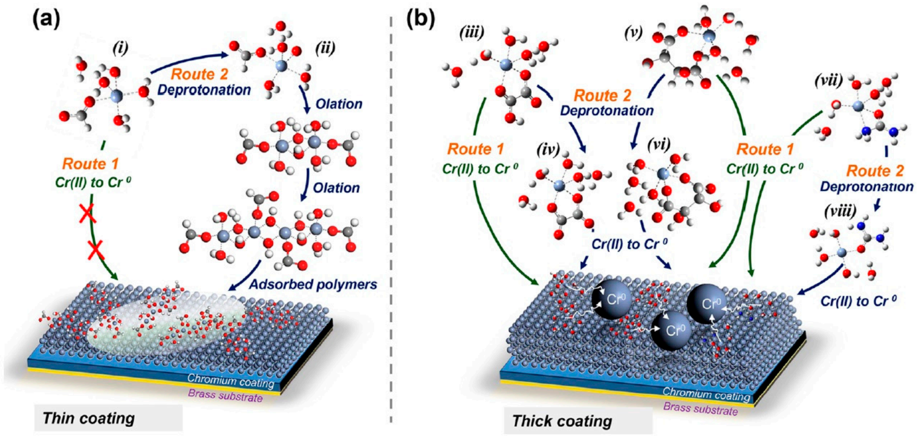

Figure 5. Two reaction routes of the Cr(II) electroreduction in trivalent chromium electrolytes containing (**a**) formic acid as a complexing agent and (**b**) the so-called ternary complexing agent. Reprinted with permission from [90]. Copyright 2020 American Chemical Society.

Thus, recent studies dedicated to the stepwise reduction of Cr(III) ions to metallic chromium have placed significant attention on exploring the details and specific characteristics of the chemistry and electrochemistry of complex Cr(III) and Cr(II) compounds.

2.2. Electrolytes Based on Ionic Liquids and Deep Eutectic Solvents Containing Trivalent Chromium Salts

2.2.1. Electrolytes Based on "Common" Ionic Liquids

Although the development of chromium plating electrolytes based on aqueous solutions of Cr(III) salts and the investigation of the kinetics and mechanism of the chemical and electrochemical reactions involved have been, and remain, important areas of research [91], recently, increased attention has been given to the processes of discharging Cr(III) ions from non-aqueous electrolytes. For example, one possible way to overcome the limitations inherent to deposition processes from aqueous solutions—and to explore additional possibilities for the electroplating of chromium—is the use of Cr(III)-containing electrolytes based on ionic liquids and their analogs. It is known that electrochemical systems based on ionic liquids offer advantages such as relatively wide "electrochemical windows" (as compared with aqueous electrolytes), non-volatility and non-flammability (unlike many organic solvents), as well as relatively high electrical conductivity and solubility of the salts of many metals [92,93]. Therefore, in recent years, the electroplating of various metals and alloys from ionic liquid electrolytes has been the subject of intensive research [94].

The patterns of chromium electrodeposition from imidazolium-based ionic liquids have been investigated using derivatives such as 1-butyl-3-methylimidazolium tetrafluoroborate [95–97], 1-butyl-3-methylimidazolium bromide [98,99], and 1-ethyl-3-methylimidazolium bisulfate [100], as well as 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, and 1-hexyl-3-methylimidazolium chloride [101]. In all cases, Cr(III) ions were introduced into the electrolyte in the form of chromium(III) chloride.

Similar to aqueous electrolytes, the electroreduction of Cr(III) ions in imidazolium-based ionic liquids proceeds stepwise with the formation of intermediates, Cr(II) ions [96–100]. However, the electrochemical process can be complicated by the cathodic reduction of internally coordinated water molecules, leading to the accumulation of OH^- ions near the electrode surface and chemical decomposition of $BF_4{}^-$ anions [95], as described by the following reactions:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \tag{20}$$

$$BF_4{}^- + 4OH^- \leftrightarrow B(OH)_4{}^-. \tag{21}$$

In this case, the source of water molecules is the crystalline hydrate form of chromium (III) chloride salt. However, the rate of these reactions or their current efficiency was not quantitatively determined in the study [95].

Some quantitative parameters of the electrochemical discharge processes of Cr(III) ions have been determined in separate studies. For instance, Eugenio et al. [97] employed cyclic voltammetry and found that the diffusion coefficient of Cr^{3+} ions in $[BMIm][BF_4]$-based solutions varied from 3.13×10^{-8} to 25.8×10^{-8} $cm^2\ s^{-1}$ over the temperature range of 303 K to 358 K. These values are significantly lower than those observed in aqueous solutions. The activation energy for diffusion was approximately 24 kJ mol^{-1}. A transfer coefficient for the discharge of Cr(III) to Cr(II) was calculated, and it was found to be $\alpha = 0.26$. He et al. [98] reported a diffusion coefficient of Cr^{3+} ions in [BMIM]Br-based solutions as 22.30×10^{-6} $cm^2 \cdot s^{-1}$ at 358 K, with a transfer coefficient for the discharge of Cr(III) to Cr(II) of $\alpha = 0.276$. For $[EMIM]HSO_4$-based solutions, the diffusion coefficient was found to be in the range of 2.60×10^{-7} to 15.99×10^{-7} $cm^2\ s^{-1}$ over the temperature range of 303 K to 358 K [100].

As for the kinetics of the second stage of reduction (direct deposition of metallic chromium) from ionic liquids, some patterns of electrocrystallization kinetics have been investigated in specific studies. For example, it has been shown that deposition in $[BMIm][BF_4]$-assisted systems occurs through an instantaneous nucleation mechanism [98,99]. Interestingly, when $[EMIm]HSO_4$ is used as an electrolyte for chromium deposition, the electrocrystallization follows the progressive nucleation model at low cathodic overpotentials, whereas the mechanism of instantaneous 3D nucleation with diffusion-controlled growth dominates at high overpotentials [100].

2.2.2. Electrolytes Based on Deep Eutectic Solvents

Over the past two decades, the so-called deep eutectic solvents (DESs) have been proposed as analogs to ionic liquids, as they share many characteristics and properties of "common" room-temperature ionic liquids [102–104]. DESs are systems formed by a eutectic mixture of a Lewis or Brønsted acid and base, both organic and inorganic in nature. Typically, DES components consist of large, asymmetric ions, characterized by a low lattice energy and, therefore, a low melting point. DESs are usually obtained by mixing a quaternary ammonium salt (most commonly choline chloride) with metal salts (usually halides) or hydrogen bond donors (organic acids, amides, etc.) [102–104]. The delocalization of electric charge resulting from the formation of hydrogen or donor-acceptor bonds leads to a decrease in the mixture's melting temperature compared to the melting temperatures of individual components and the electrolytic dissociation of the mixture's constituents.

Currently, DESs are considered promising solvents for various processes and technologies [102,105]. Deep eutectic solvents are highly productive and promising for applications in the field of electrochemistry, particularly for metal electrodeposition [102,106–108]. DES-based systems can be successfully utilized for the deposition of chromium coatings as well.

Abbott et al. [109] first described the synthesis of a deep eutectic solvent containing a eutectic mixture of choline chloride and chromium(III) chloride hexahydrate. It was shown that the synthesized Cr(III)-containing DES can be used for chromium electrodeposition. This process achieves relatively high current efficiency (up to 90%), and the deposited coatings exhibit crack-free characteristics and sufficient adhesion to the substrate. Regarding the specific kinetics of electrode reactions, an anomaly was observed on the voltammetric curve, which involved a sharp decrease in the cathodic current for the reduction of Cr(III) to Cr(II) on a platinum microelectrode at $E < -0.5$ V (Figure 6). This was attributed to surface passivation due to the deposition of sparingly soluble Cr(II) intermediate particles on the surface.

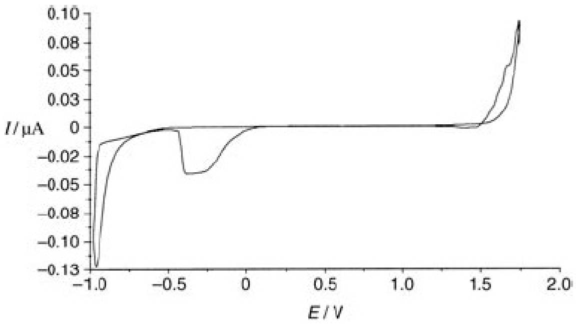

Figure 6. Cyclic voltammogram recorded on a platinum microelectrode in a liquid mixture containing choline chloride and $CrCl_3 \cdot 6H_2O$ (1:2 mol.) at 60 °C and a scan rate of 0.02 V s^{-1}. Reprinted from [109] Copyright 2004, with permission from John Wiley and Sons.

Abbott et al. [110] also obtained a eutectic mixture of urea and chromium(III) chloride hexahydrate, which is liquid at room temperature. It was found that in this ionic liquid, trivalent chromium exists predominantly in the form of a complex cation $[CrCl_2(OD)_4]^+$, where OD represents "oxygen donor ligands" (as referred to by the authors), which can be either urea or water. It was shown that the current efficiency of the electrolytic chromium deposition reaction from such DES is approximately 65–74%, significantly higher than the values typically observed in "traditional" aqueous electrolytes, despite the presence of water molecules originating from the crystalline hydrate form of the salt. It was established that the chromium deposition occurs through sequential processes of one-electron transfer (Cr^{3+}/Cr^{2+}) and two-electron transfer (Cr^{2+}/Cr^0).

Ferreira et al. [111] investigated the electrochemical properties of an ionic liquid containing choline chloride and chromium(III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) in a molar ratio of 2.5:1 with an additional 20 wt.% of water. It was demonstrated that the electrochemical reduction of Cr(III) ions occurs in two sequential stages: Cr(III) → Cr(II) and Cr(II) → Cr(0), where the rate of the first stage is diffusion-controlled for Cr(III) ions. Thus, compelling evidence was obtained that chromium deposition in DESs, similar to "conventional" aqueous electrolytes, proceeds stepwise through the formation of intermediates—divalent chromium ions. The nucleation stage of chromium was also studied, showing that the electrodeposition is complicated by adsorption processes and follows a 3D growth mechanism controlled by diffusion, as well as progressive nucleation with 3D growth. It was noted that the proposed electrolyte allows for depositing bright coatings with good adhesion to the substrate and does not require the use of any additional complexing agents.

The process of electrochemical nucleation of chromium on a glassy carbon electrode during metal deposition from an electrolyte based on a eutectic mixture of choline chloride and ethylene glycol has been experimentally investigated [112]. A kinetic model has been developed that takes into account the steps of diffusion of Cr(III) ions to the electrode surface, adsorption, charge transfer, 3D nucleation, and crystal growth. It has been found that the presence of water impurities in the DES significantly affects the kinetics of nucleation and crystal growth.

In the work [113], the main focus was also on establishing the patterns of electrochemical nucleation kinetics of chromium from DES based on choline chloride and ethylene glycol. Within the confirmed mechanism of diffusion-controlled 3D nucleation, quantitative parameters of the model were determined. This study made one of the few attempts to determine the kinetic parameters of the electrochemical deposition reaction of chromium. Specifically, it was calculated that the exchange current density for the Cr(III)/Cr(0) transfer process is 6.783×10^{-4} mA cm^{-2}, which, according to the authors, indicates an irreversible nature of the deposition reaction. However, it is not entirely clear to which electrochemical step the calculated current density corresponds, considering the stepwise nature of charge transfer in this system.

The physical and chemical properties of ionic liquids composed of a mixture of chromium(III) chloride hexahydrate and choline chloride (2:1) with the addition of oxalic acid have been extensively characterized [114]. Voltammetric analysis confirmed the stepwise nature of the electrochemical deposition process of chromium coatings and revealed a significant influence of the metal-substrate nature on the kinetics of the chromium ion reduction. Specifically, on a platinum electrode, the continuous growth of the cathodic current was observed in voltammograms during linear potential scanning, which is attributed to the direct discharge of Cr^{3+}-containing particles. On a copper substrate, when scanning the electrode potential in the cathodic direction, a distinct two-step reduction of Cr(III) ions is evident. The first peak (or plateau) corresponds to the process of soluble Cr(III) → insoluble Cr(II) species, and the subsequent increase in the cathodic current is related to the reaction of Cr(II) → Cr(0).

Currently, significant attention is being given to the investigation of the influence of water additives on the physicochemical and electrochemical behavior of DES-based systems, as the addition of a certain amount of water as an additional hydrogen bond donor allows for flexible control over various properties of these ionic liquids [115–117]. McCalman et al. [118] determined the compositions of complex particles of trivalent chromium ions depending on the composition of the liquid ionic mixture containing chromium(III) chloride, water, and choline chloride. It was found that the coordination number of the central ion in Cr^{3+} complexes is six. On average, the metal ion coordinates with two to five water molecules and one to four chloride ions in the inner sphere. The average number of water molecules increases with increasing total water concentration, while the number of Cl^- ions increases with increasing choline chloride concentration. The obtained voltammograms showed complex and ambiguous dependencies of the current density corresponding to the discharge of trivalent chromium ions on the electrolyte composition.

The cycle of works [119–122] was dedicated to the investigation of the physicochemical properties and electrochemical behavior of ionic liquids containing chromium(III) chloride, choline chloride, and water additives in molar ratios of 1:0.5:x and 1:2.5:x, respectively (where x = 6, 9, 12, 15, or 18), as well as establishing the patterns of chromium coatings electrodeposition from these systems. It was shown that an increase in the water content results in a decrease in density, surface tension, and viscosity, as well as an increase in the electrical conductivity of the ionic liquid, which is important and favorable for the potential practical application of these electrolytes [119,120]. It was proven that the mechanism of ion migration by hopping to vacancies (“holes”) is preserved upon the introduction of water. Therefore, these systems should be considered as “true” ionic liquids rather than concentrated aqueous solutions. It was determined that simultaneous stepwise discharge of Cr(III) ions occurs in the investigated DESs along with electrochemical hydrogen evolution and incorporation of carbon into the electrodeposits, leading to the deposition of amorphous Cr–C alloys with a metal content of approximately 80 wt.% [121]. The introduction of water into the electrolyte leads to a sharp decrease in the current efficiency of the electroplating process and deterioration of the appearance of the deposits. Typical voltammetric curves recorded at different water contents in the electrolytes are shown in Figure 7. These curves exhibit a cathodic peak at potentials around −0.5 to −0.9 V, corresponding to the incomplete reduction of Cr(III) ions with the formation of Cr(II) intermediates. With further cathodic polarization, an increase in the cathodic current associated with simultaneous chromium deposition and hydrogen evolution is observed. On the reverse scan, a self-intersection appears on the polarization curve (formation of a loop), which is typical of the nucleation and growth of metals on a foreign substrate. Two weak current waves are formed on the anodic scan at approximately −0.4 V and approximately 0 V, corresponding to the stripping dissolution of the chromium metal phase deposited on the previous cathodic scan and the oxidation of Cr(II) ions to Cr(III), respectively. Current waves at potentials greater than 1 V on the cyclic voltammograms are associated with electrode processes involving components of DESs, rather than chromium ions [123]. From the obtained voltammetric curves, it can be observed that as the water content increases in the system $CrCl_3 + 2.5ChCl + xH_2O$ (i.e., with increasing x) there is an increase in the limiting diffusion current for the reduction of Cr(III) to Cr(II). This is likely related to an increase in the diffusion coefficient due to a decrease in the electrolyte viscosity. In principle, this would also promote faster discharge of the intermediates to the metallic state, i.e., an increase in the rate of chromium deposition. However, with increasing water content, the hydrogen evolution process intensifies, which reduces the current efficiency of the chromium deposition reaction and leads to the occurrence of olation and formation of insoluble Cr(III) hydroxides. These species block the electrode surface and become incorporated into the structure of the deposited coating, deteriorating its properties. Thus, the addition of water to the electrolyte has both positive and negative consequences regarding the chromium deposition reaction in DESs, and a certain compromise (optimal) water content should be found.

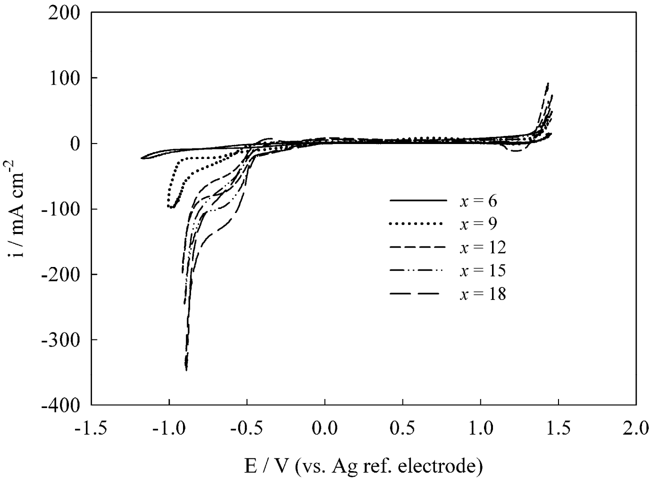

Figure 7. Cyclic voltammograms obtained on a platinum electrode in electrolytes containing $CrCl_3 + 2.5ChCl + xH_2O$ (temperature 70 °C, sweep rate 0.1 V s^{-1}) [121].

The influence of water additives on the electroreduction of chromium(III) ions in deep eutectic solvents consisting of an eutectic mixture of ethylene glycol and choline chloride was also studied [124]. Figure 8 illustrates a series of cyclic voltammograms obtained at different water contents. It is evident that increasing the water content, similar to the DES investigated in the study mentioned earlier [121], accelerates the discharge reaction of chromium(III) ions. In the study [124], kinetic parameters of the discharge reaction of chromium ions, such as transfer coefficients, standard rate constants, diffusion coefficients, activation energies of diffusion and charge transfer, were determined and thoroughly analyzed. However, it should be noted that the kinetic data obtained in these studies primarily pertain to the initial step of the discharge process, Cr(III) → Cr(II), while the kinetics and mechanism of the discharge of divalent chromium ions, including the influence of water, remain poorly understood at present.

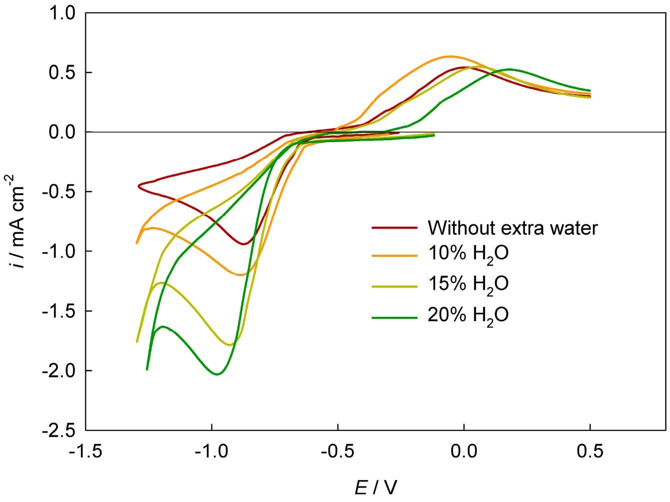

Figure 8. Voltammograms obtained in electrolyte containing 0.05 mol dm^{-3} $CrCl_3 \cdot 6H_2O$ in eutectic mixture of ethylene glycol and choline chloride at different contents of extra water (temperature 323 K, scan rate 0.050 V s^{-1}) Reprinted from [124], Copyright 2020, with permission from Elsevier.

Mejía-Caballero et al. [125] were the first to investigate the influence of forced convection intensity on the kinetics and mechanism of deposition from Cr(III)-DES-based baths. In order to do so, they examined the effect of the rotation speed of a glassy carbon rotating disk electrode on the discharge of chromium(III) ions from the eutectic mixture of choline chloride and ethylene glycol. It was demonstrated that the coating consists of chromium and oxygen (chromium is present in both metallic form and as compounds $Cr(OH)_3$ and Cr_2O_3), with the oxygen content in the chromium-based coating increasing with higher electrode rotation speeds. The obtained results were adequately interpreted within the framework of the developed theoretical concept.

Regarding the influence of surfactants on the discharge of chromium ions in DESs, this issue remains largely unexplored. Barzinjy [126] characterized the chromium plating process from an electrolyte based on a DES which contained chromium (III) chloride hexahydrate, urea, as well as the additives of acetylacetone and water. It was demonstrated that the addition of acetylacetone as a surfactant to the electrolyte affects the nucleation processes and contributes to a significant reduction in the surface roughness of the coatings. However, the effect of acetylacetone additives on the kinetics of electrode reactions has not been studied.

3. Conclusions

This study provides a comprehensive review and systematic analysis of the literature data concerning the kinetics and mechanisms of reactions occurring during the electrodeposition of chromium coatings from electrolytes based on trivalent chromium salts. These electrolytes serve as a safer alternative to highly hazardous chromium plating technologies that employ compounds of hexavalent chromium.

The key characteristic of the mechanism of electrochemical reduction of Cr(III) ions is its stepwise nature, which involves the formation of intermediates, specifically divalent chromium ions. This stepwise process is common to both aqueous electrolytes and ionic liquids, including deep eutectic solvents. The formation of these intermediates is an essential part of the overall reaction pathway, and understanding their behavior is crucial for elucidating the kinetics and mechanisms of chromium electrodeposition.

The literature data regarding the influence of organic additives on the kinetics and mechanism of chromium electrodeposition are characterized in this study, along with some patterns of the co-deposition of metalloids (such as carbon or phosphorous) with chromium. It is noted that organic additives incorporated into chromium plating electrolytes can act as "conventional" surfactants, selectively adsorbing at specific phase boundaries, and also form complex compounds with chromium(II) and chromium(III) ions, which determine the peculiarities of the mechanism and kinetics of the electrode reactions taking place.

An important characteristic of the stepwise process of Cr(III) ion discharge is that this electrochemical reaction is almost always accompanied by concurrent electrochemical hydrogen evolution. This not only reduces the current efficiency of the chromium deposition reaction but also leads to localized pH increase in the vicinity of the electrode and the formation of hydroxide compounds and hydroxo-complexes of Cr(III) and Cr(II). These factors significantly influence the kinetics of cathodic transformations.

Determining the influence of various organic and inorganic additives (such as complexing agents, surfactants, metalloid sources, water-soluble polymers, buffer additives, etc.) is an important task both for understanding the kinetic laws and for the practical application of these systems. Recent literature analysis indicates that this issue remains relevant, and progress can be achieved by considering multiple additives simultaneously rather than individual ones. By studying the combined effects of multiple additives, significant advancements can be made in elucidating the mechanisms and kinetics of electrodeposition processes. Additionally, this approach can provide valuable insights for optimizing the performance and properties of the deposited coatings.

The literature data indicate that one of the most relevant and promising directions for the development of new electrochemical chromium plating processes is the utilization of ionic liquids and, in particular, their analogs, known as deep eutectic solvents (DESs). However, progress in this direction is significantly hindered by the insufficient understanding of the peculiarities and details of the kinetics and mechanisms involved in these electrolytes. This lack of knowledge underscores the importance of further research in order to fully explore the potential of such electrochemical systems and uncover their underlying mechanisms. Advancements in the understanding of these processes will pave the way for the development of improved and sustainable chromium plating techniques.

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