

SHORT
COMMUNICATIONS

Effect of Formic Acid on the Electroreduction of Compounds of Hexavalent Chromium

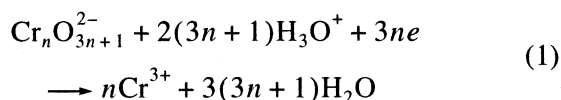
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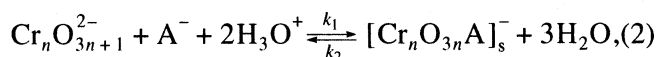
INTRODUCTION

Hydroxy anions of Cr(VI) belong among the difficultly reducible anions. Discharge kinetics of such anions were thoroughly explored at the dropping mercury electrode mainly in alkaline and neutral solutions [1–4]. Studying the electroreduction in more acidic and more chromium-concentrated electrolytes is complicated by the fact that compounds of Cr(VI) strongly oxidize most of the electrode materials, leading to dissolution and passivation of them. Moreover, in such electrolytes, the electrochemical process



becomes severely affected by the nature and concentration of some compounds-catalysts of a predominantly anionic character [5, 6].

We showed in [7] that the role played by additives that accelerate reduction of compounds of Cr(VI) may amount to their participation in the formation of electrochemically active surface complexes in the chemical reaction



which precedes the discharge. We also noted in [7] that, similar to such compounds as H_2SO_4 , HF, etc., formic acid can also facilitate reaction (1). In recent years, the HCOOH influence on the Cr(VI) electroreduction has been the subject of a lively discussion, largely in connection with its favorable effect on properties of the metal coating [7–13].

In this work, we investigate voltammetrically cathodic processes at the gold and chromium electrodes in chromic-acid electrolytes containing sulfuric and formic acids. Note that the Cr electrode surface is susceptible to formation of films comprising various oxide-hydroxide compounds.

PROCEDURE AND RESULTS OF THE EXPERIMENTS

The study was conducted on the gold and chromium electrodes. The latter was prepared from a copper foil

($S = 0.5$ or 1 cm^2) chromium-plated in $2.5 \text{ M CrO}_3 + 0.025 \text{ M H}_2\text{SO}_4$ at 35 A dm^{-2} and 325 K . The thickness of the Cr coating was about $5 \mu\text{m}$. The rest of the procedure is identical to that described [7]. Let us note in passing that all the polarization measurements are taken at 298 K , and all the potentials are given with respect to NHE.

The principal process at the gold electrode in 1 M CrO_3 is hydrogen evolution (curve 1 in Fig. 1). Under these conditions, electroreduction of hydroxy anions of Cr(VI) becomes noticeable only after sulfuric or formic acid is added into the electrolyte (curves 2–5 in Fig. 1).

Upon reaching the hydrogen evolution range, regions of periodic oscillations of the current appear in voltammograms recorded at a potential scan rate of 5 mV s^{-1} . The regions are shown by dashed lines in curves 3 and 4 of Fig. 1. The amplitude of the oscillations is $40\text{--}50 \text{ mA cm}^{-2}$ and the frequency is approximately 0.5 Hz . A fresh peak occurs in voltammograms recorded at 100 mV s^{-1} , which is followed by an abrupt current decrease. Introducing HCOOH into a sulfate-containing electrolyte makes almost no impact on the voltammograms and the limiting current of the Cr(VI) reduction (curve 4 in Fig. 1).

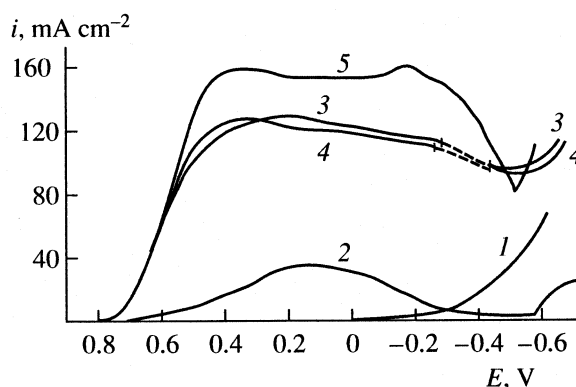


Fig. 1. Cathodic voltammograms for the Au electrode in (1) 1 M CrO_3 , (2) $1 \text{ M CrO}_3 + 0.34 \text{ M HCOOH}$, (3, 5) $1 \text{ M CrO}_3 + 0.05 \text{ M H}_2\text{SO}_4$, and (4) $1 \text{ M CrO}_3 + 0.05 \text{ M H}_2\text{SO}_4 + 0.34 \text{ M HCOOH}$, obtained at potential scan rates of (1–4) 5 and (5) 100 mV s^{-1} .

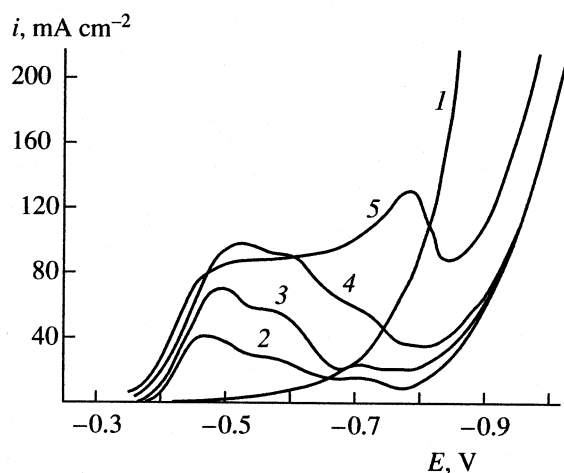


Fig. 2. Cathodic voltammograms for the Cr electrode in (1) 1 M CrO_3 , (2) 1 M CrO_3 + 0.02 M H_2SO_4 , (3) 1 M CrO_3 + 0.05 M H_2SO_4 , (4) 1 M CrO_3 + 0.08 M H_2SO_4 , and (5) 1 M CrO_3 + 0.05 M H_2SO_4 + 0.34 M HCOOH , obtained at 5 mV s^{-1} .

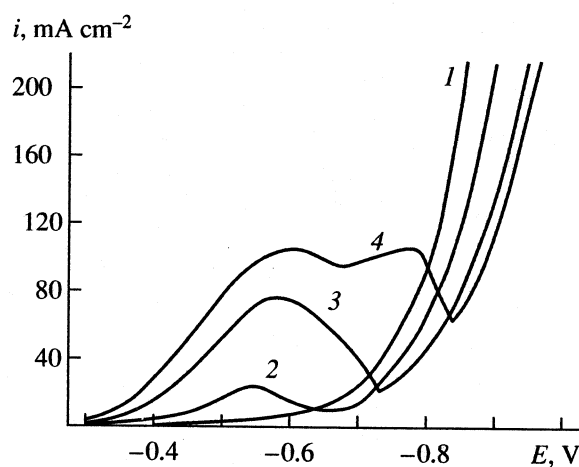


Fig. 3. Cathodic voltammograms for the Cr electrode in 1 M CrO_3 solutions containing (1) 0, (2) 0.45, (3) 0.68, and (4) 1.13 M HCOOH , obtained at 5 mV s^{-1} .

Hydroxy anions undergo almost no reduction in the aqueous solution of CrO_3 at the Cr electrode. The only electrode process in the circumstances is hydrogen evolution (curve 1 in Fig. 2). Introducing H_2SO_4 into the electrolyte gives rise to a current peak in the voltammograms (curves 2–4 in Fig. 2), which corresponds to reaction (1). As the potentials of electroreduction of Cr(VI) and hydrogen at the Cr electrode are close, reaction (1) at the Cr electrode is accompanied by discharge of the hydronium ions. The cathodic current densities in the maximum and minimum of the i vs. E curve, i_{max} and i_{min} , increase with the H_2SO_4 concentration. The voltammogram, recorded in the electrolyte containing sulfuric and formic acids simultaneously, contains a distinct plateau of the limiting current of the Cr(VI) reduction (curve 5 in Fig. 2). Similar curves are obtained in the chromium-plating electrolytes containing formic acid (Fig. 3). Reaction (1) accelerates with the growing concentration of HCOOH (i_{max} and i_{min} increase).

DISCUSSION

According to our results, HCOOH , like H_2SO_4 , catalyzes the Cr(VI) reduction at the gold and chromium electrodes. However, despite higher contents of HCOOH compared with H_2SO_4 (about 0.3 and 0.05 M respectively), the values of i_{max} in formate-containing electrolytes are lower than in sulfate-containing solutions. This means that the catalytic activity of HCOOH is noticeably lower than that of H_2SO_4 . Apparently, the rate constant of reaction (2) pertaining to the formation of electroactive complexes with formic acid is smaller than in the case of sulfuric acid. This may explain why adding HCOOH into a sulfate-containing electrolyte

fails to affect the voltammogram's shape and i_{max} (curves 3, 4 in Fig. 1).

The kinetics intrinsic to electroreduction of compounds of Cr(VI) at the Cr electrode are unique in that the apparent value of cathodic polarization is very large, reaching -1.5 to -1.8 V at $E^0 = 1.33$ V for $\text{Cr}_2\text{O}_7^{2-}$, $14\text{H}^+/2\text{Cr}^{3+}$, $7\text{H}_2\text{O}$. Note that, according to [14], "it is usually impossible to reach overvoltages in excess of 0.2 to 0.3 V in redox systems."

Apparently, the reduction $\text{Cr(VI)} + 3e \rightarrow \text{Cr(III)}$ proceeds at the Cr electrode covered by a passivating oxide layer, and a considerable part of the potential drop measured occurs is the surface oxide film. Similar ideas were put forth in [15]. However, we believe that the oxide layer remains at the Cr electrode surface even if catalysts are present in chromic-acid electrolytes. The cathodic polarization for process (1) on the gold electrode free of passivating films [7] is significantly smaller.

The Cr(VI) electroreduction is hampered not only by the passivating oxide layers. The process is also inhibited by the formation of colloidal oxide-hydroxide compounds of chromium of an intermediate valence [15–17] that block the electrode surface. This phenomenon results from the alkalization of the near-electrode layer, which is caused by the occurrence of reaction (1) and discharge of the hydroxonium ions and by the low solubility product of hydroxy compounds of Cr(III).

The waves for reduction of Cr(VI) and H_3O^+ at the gold electrode are separated (Fig. 1). This electrode becomes blocked only in the narrow potential region, where these two processes occur at commensurate rates. As a result, the voltammogram recorded at 100 mV s^{-1} exhibits an abrupt current decrease at about

-0.5 V. The current oscillations at 5 mV s^{-1} are associated with the concurrent processes of the formation of a blocking film of hydroxide compounds and its dissolution in the chromic-acid electrolyte.

Once the limiting current of reaction (1) at the Cr electrode is reached, the hydrogen evolution rate rises dramatically, which results in alkalization of the near-electrode layer of the electrolyte. Therefore, the maximums in the pertinent voltammograms are, as a rule, connected with the blocking of the electrode surface by a film of chromium hydroxide [15, 16], rather than with the exhaustion of kinetic possibilities of the heterogeneous chemical reaction that precedes the discharge and yields electroactive complexes [7]. As the concentration of H_2SO_4 or HCOOH increases, reaction (2) accelerates and the formation of hydroxy compounds at the cathode becomes hampered by the fact that both H_2SO_4 and HCOOH bind Cr(III) into soluble complex compounds. Moreover, HCOOH acts as a buffer additive and prevents the pH growth in the near-electrode layer. Eventually, this leads to the increase in i_{max} and i_{min} observed experimentally. In some cases, the formation of poorly soluble hydroxides is suppressed so much that the plateau of the reaction $\text{Cr(VI)} + 3e \rightarrow \text{Cr(III)}$ emerges in the voltammogram for the Cr electrode (curve 5 in Fig. 2).

The current wave in voltammograms at -0.75 to -0.80 V, which is clearly seen in curve 5 of Fig. 2 and curve 4 of Fig. 3, is probably associated with a drastic increase in the partial rate of hydrogen evolution. At potentials below -0.8 V, the cathodic current starts to increase again, and the discharge of H_3O^+ and Cr(VI) via reaction (1) becomes accompanied by the deposition of metallic chromium.

As a rule, at room temperature, the chromium deposition from the HCOOH -free electrolytes yields gray coatings; at $c_{\text{HCOOH}} > 0.22 \text{ M}$, the coatings become bright [11]. According to [5], bright coatings can be produced in a limited interval of the electrode coverages with sol of chromium hydroxide. This means that the colloidal film at the cathode must not be continuous. In chromic-acid electrolytes containing no organic additives, these conditions are usually realized at temperatures exceeding 313 K. Introducing HCOOH into the electrolyte results in a partial disruption (dissolution) of the film of hydroxide compounds; as a result, bright coatings form even at 288–293 K. Similar ideas were put forth in [10].

It is chromium-carbon alloys that form at the cathode in chromium-plating electrolytes based on both Cr(VI) and Cr(III) and containing HCOOH [18, 19]. In this case, HCOOH is the source of carbon in the coatings. The enhanced corrosion resistance of carbon-containing coatings [13] is connected exactly with the fact that they contain carbon. In addition, the interaction between chromium and carbon in the course of the solid phase formation results in the production of an amorphous metallic material.

In chromium coatings containing a relatively large amount of carbon (1–4 wt % or 4.2–15.3 at. %), the oxygen content does not exceed 0.2 wt % or 0.65 at. % [19]. Therefore, it seems unlikely that the carbon incorporation into the coating amounts to a mere occlusion of adsorbed molecules of HCOOH or ions HCOO^- by the growing deposit [8, 10]. During a codeposition with chromium, HCOOH probably undergoes an electrochemical reduction. This problem calls for a thorough investigation and we will consider it in the future.

CONCLUSION

Thus, it is established that formic acid in chromic-acid electrolytes catalyzes electroreduction of Cr(VI) compounds at the gold and chromium electrodes. The catalytic activity of HCOOH towards this reaction is weaker than that of H_2SO_4 . Owing to its complexing and buffer action, HCOOH prevents formation of chromium hydroxide in the near-electrode layer, thus facilitating production of bright coatings.

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