



Cyclic voltammetry study of trivalent basic chromium sulphate electrolytes contaminated with sulphite

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ABSTRACT

The discovery of sulphite in basic chromium sulphate, typically used as the source of Cr(III) ions in trivalent chromium electrolytes, sparked an investigation into the effects of this species on the reactions at a platinum electrode in a Cr(III)-formate electrolyte. The specific adsorption and oxidation-reduction reactions of sulphite were mapped using cyclic voltammetry and linked to competitive adsorption between sulphite, formic acid and the Cr(III)-formate complex.

It was found that sulphite adsorption and reduction/oxidation dominates the cyclic voltammogram-metric response. Formic acid oxidation is completely inhibited as long as sulphite is present at the surface.

A feasible way of removing any sulphite from a contaminated electrolyte is by applying a prolonged reductive current.

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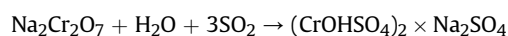
1. Introduction

In response to REACH legislation, the plating industry is gradually converting from hexavalent to trivalent chromium electrolytes [1–3]. Obviously, oxidation of Cr(III) to Cr(VI) at the anode during the plating process must be ruled out [4–15]. In a recent study, we reported that in trivalent chromium electrolytes with formate as complexing agent, Cr(VI) is formed at a platinum anode, but not at a titanium anode with a mixed metal oxide (MMO) coating comprising iridium oxide (IrO₂) and tantalum oxide (Ta₂O₅) [15].

Using cyclic voltammetry combined with On-Line Electrochemical Mass Spectrometry (OLEMS) measurements, it was observed that at platinum the characteristic ‘surface explosion’ peak due to oxidation of formate to CO₂ is completely suppressed when basic chromium sulphate ((CrOHSO₄)₂ × Na₂SO₄) is added to a formate solution. This was attributed to adsorption of the Cr(III)-formate complex to the platinum surface. However, after publication of ref. 15, the CO₂ surface explosion peak was measured in a Cr(III) electrolyte sample from a plating line, thus in conflict with our previous conclusions. Additionally, we observed that the

current efficiency of the chromium plating process had strongly improved after prolonged use of the trivalent chromium bath. Both findings sparked an investigation into the purity of the basic chromium salt that was used for our study.

Basic chromium salt is industrially prepared by the reduction of Cr(VI) in the form of sodium dichromate to Cr(III) with SO₂ [16]:



An excess of sulphur dioxide is required to ensure chromium is fully reduced to the 3 + oxidation state. Chemical suppliers use a second reaction to remove the residual sulphur dioxide. However, if present, excess SO₂ will result in the formation of sulphurous acid (H₂SO₃), which may in turn form sulphite anions:



Having become aware of the possible presence of sulphite or related species in trivalent chromium electrolytes, it was decided to investigate whether the cyclic voltammetry measurements in our previous study might be affected by a sulphite contamination of the basic chromium salt.

We believe this study is also relevant to other chromium plating studies, as basic chromium sulphate is the common source of Cr(III) ions in trivalent chromium electrolytes, and therefore the effect of

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traces of sulphite in the electrolyte may have to be considered in other systems as well. From a more scientific point of view, our study gives a better insight into the effect of competitive adsorption on reactivity and selectivity in multi-component electrolytes.

2. Experimental

2.1. Electrolytes

All chemicals used for preparing the electrolytes were p.a. grade except for the basic chromium(III) sulphate salt ((CrOH-SO₄)₂·Na₂SO₄·H₂O) with trade name Trisurfin[®] supplied by Soda Sanayii A.Ş.

All electrolytes contain 900 mM Na₂SO₄ as supporting salt and were adjusted to pH 2.8 at 25 °C by adding sulphuric acid.

2.2. Cyclic voltammetry measurements

The working electrode was a mirror polished platinum Rotating Disk Electrode (RDE) tip from Pine Instrument Company with an outer diameter of 5 mm.

Prior to the measurements, the Pt RDE was cleaned in a 0.1 M H₂SO₄ electrolyte by repetitive potential scans between the onset of hydrogen evolution on the cathodic side and oxygen evolution on the anodic side until a stable cyclic voltammogram (CV) was obtained.

The potential was controlled by a Metrohm Autolab PGSTAT302N potentiostat. All potentials are reported vs. an Ag/AgCl/KCl (sat'd) electrode. A fine-meshed circular platinum gauze with a diameter of 30 mm served as counter electrode.

A glass cell with an integrated water jacket connected to a LAUDA Ecoline E 100 circulation thermostat was used to keep the electrolyte at 50 °C.

All cyclic voltammograms were recorded with a rotation rate of 9 rps and a scan rate of 100 mV s⁻¹.

2.3. Electrolysis experiments

To study the purification process of the Cr(III) electrolyte and the removal of sulphite in time, electrolysis experiments were executed in a flow channel cell. To study the oxidation resp. reduction of sulphite, electrolysis experiments were done in a two-compartment cell with separated electrodes.

2.3.1. Flow channel cell

The flow channel cell is designed for producing A4 sheet samples under controlled mass transfer conditions. The electrolyte volume is 200 l and the channel gap is 10 mm. The flow rate was 8 m³ h⁻¹ corresponding to a liquid velocity in the channel cell of 1.1 m s⁻¹.

The anode was titanium with a catalytic mixed metal oxide (MMO) coating comprising iridium oxide (IrO₂) and tantalum oxide (Ta₂O₅) supplied by MAGNETO special anodes B.V. The catalytic coating thickness was 5 µm. A low-carbon mild steel sheet (NEN-EN 10205) with a surface area of 300 mm × 200 mm and a gauge of 0.183 mm was used as the cathode. During electrolysis, the electrolyte temperature was kept at 50 °C.

An SM 30-100 D Power Supply from Delta Elektronika was used for applying the current.

2.3.2. Two-compartment cell

Both compartments were separated by a glass frit allowing migration of ions, but preventing convective mixing of the catholyte and anolyte. A low-carbon mild steel sample (20 mm × 20 mm) of which one side was insulated by means of

tape was used as cathode and titanium with an MMO coating (see previous section) was used as anode. The electrolyte in the compartment holding the cathode was moderately agitated by a magnetic stirrer. The volume of the catholyte was 100 ml.

During electrolysis, the electrolyte temperature was kept at 50 °C.

The current was controlled by a Metrohm Autolab PGSTAT302N potentiostat/galvanostat.

3. Results

3.1. Comparison of a fresh and a used Cr(III) electrolyte

The cyclic voltammogram (CV) of a freshly prepared Cr(III) electrolyte is given in Fig. 1 (blue curve). The oxidation of formic acid to CO₂ is clearly suppressed, which can be explained by assuming that some species is strongly adsorbed at the platinum surface. A CV was recorded of a Cr(III) electrolyte sample from a plating line after several hours of operation (Fig. 1: red curve). Clearly, this CV is very different from the CV of a fresh Cr(III) electrolyte: the characteristic features of formic acid oxidation are clearly present, especially the CO₂(g) surface explosion peak at 0.2 V in the negative-going scan.

The composition of both electrolytes is supposedly similar, so a chromium-formate complex is present in both cases. This is not in agreement with our previous hypothesis that the chromium(III)-formate complex adsorbs strongly at the platinum surface [15]. The following experiments are aimed at checking the hypothesis that sulphite is the strongly adsorbing species responsible for the changes in the CV.

3.2. Sulphite oxidation

Fig. 2 shows a cyclic voltammogram of a 900 mM sodium sulphate solution (pH 2.8) with various sodium sulphite additions. The reference graph without any sulphite shows a limiting current density plateau due to the reduction of oxygen below 0.25 V.

When sulphite is added, the current rises steeply at 0.3 V, reaching diffusion limitation at 0.5 V. At this stage, the current becomes proportional to the concentration (see inset). The current decreases at potentials above 0.9 V due to the formation of platinum oxide and/or adsorption of a sulphur containing species. The increase in oxidative current between 0.9 and 0.45 V during the

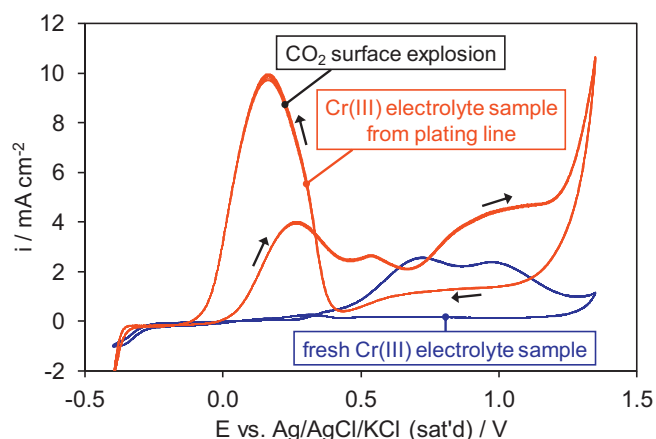


Fig. 1. Cyclic voltammograms of a fresh Cr(III) electrolyte sample (blue curve) and a Cr(III) sample from a plating line (red curve) with similar composition (900 mM Na₂SO₄ + 400 mM CrOH₂SO₄ + 600 mM HCOONa). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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