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# Oxidation reactions in chromium(III) formate electrolytes at platinum and at a catalytic mixed metal oxide coating of iridium oxide and tantalum oxide

J.H.O.J. Wijenberg[a,*], A.C.A. de Vooys[a], R. Kortlever[b], M.T.M. Koper[b]

[a] Tata Steel, Research & Development, IJmuiden Technology Centre, P.O. Box 10.000, 1970 CA IJmuiden, The Netherlands
[b] Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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ABSTRACT

In trivalent chromium plating processes, the breakdown of useful electrolyte components or the formation of hazardous products, in particular Cr(VI), at the anode is obviously undesired. In this study, the oxidation reactions in trivalent chromium electrolytes with formate as complexing agent are investigated at platinum and at a catalytic mixed metal oxide (MMO) coating comprising iridium oxide ($IrO_2$) and tantalum oxide ($Ta_2O_5$) using cyclic voltammetry combined with On-Line Electrochemical Mass Spectrometry (OLEMS) measurements.At platinum the following sequence of reaction steps is proposed (all potentials vs. SCE):

1. Oxidative adsorption of $[Cr(HCOO)(H_2O)_5]^{2+}$, reversible at −0.4 V;
2. $CO_2$ evolution from the Cr(III)-formate complex above +0.4 V;
3. Further oxidation to $HCrO_4^-$ with simultaneous $CO_2$ and $O_2$ evolution above +1.2 V.

Cr(VI) formation also occurs in the absence of formic acid, i.e. when only $Cr(H_2O)_6^{3+}$ is present in the electrolyte.

At a catalytic MMO coating the adsorption step is absent, as well as any subsequent oxidation of the Cr (III)-formate complex. This suggests that adsorption of the Cr(III) complex is required for Cr(VI) formation.

MMO electrodes allow a safe usage of the electrolyte for industrial applications, whereas platinum electrodes do not.

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## 1. Introduction

Electrolytic Chromium Coated Steel (ECCS) is used extensively in the packaging industry for the production of cans and many other components that do not have to be welded, such as ends, lids, crown corks, twist-off caps, aerosol bottoms and tops. ECCS consists of a thin gauge (0.13–0.49 mm) low carbon steel substrate with a very thin coating comprising a base layer of chromium metal (50–100 mg $m^{-2}$) and a top layer of chromium oxide (7–35 mg $m^{-2}$) [1–3].

ECCS is produced in continuous steel strip plating lines using chromium acid electrolytes [1]. To comply with occupational health and safety regulations, the toxicity of Cr(VI) requires an expensive exhaust system to capture any aerosols being released during electrolysis and also a complex waste water treatment of the effluents.

The use of Cr(VI) will be restricted within Europe in 2017 due to REACH (an acronym for Registration, Evaluation, Authorisation & restriction of CHemicals) legislation [4].

In response to REACH legislation, a trivalent chromium electrolyte with formate as complexing agent has recently been developed for the production of ECCS [5]. In the presence of water, Cr(III) ions will form a very stable hexa-aqua complex ($Cr(H_2O)_6^{3+}$), which is difficult to reduce to Cr-metal [6–10]. When formate is added to the electrolyte one of the $H_2O$ ligands in this complex is exchanged with a formate ion resulting in the formation of a much weaker $[Cr(HCOO)(H_2O)_5]^{2+}$ complex [6–10].

One major concern addressed in many scientific papers and patents on trivalent chromium plating is the possible oxidation of Cr (III) to Cr(VI) at the anode [6,11–17]. Typical anode materials used for chromium deposition processes from trivalent chromium electrolytes are carbon or platinised titanium anodes as described by Ward

* Corresponding author. Tel.: +31 251 498714.
*E-mail address:* jacques.wijenberg@tatasteel.com (J.H.O.J. Wijenberg).

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and Christie [11]. Also, metals coated with a pure metal oxide, e.g. iridium or ruthenium oxide, or a mixed metal oxide (MMO), e.g. iridium/ruthenium or iridium/tantalum oxide are used [17].

The objective of this study is both academic and industrial. The academic objective is to understand the reaction mechanism for the oxidation reactions in trivalent chromium electrolytes with formate as complexing agent at platinum and a catalytic mixed metal oxide (MMO) coating comprising iridium oxide ($IrO_2$) and tantalum oxide ($Ta_2O_5$). This knowledge is then used for the industrial objective, which is to determine which anode material is most suitable for this electrolyte.

Part of this work has formed the scientific basis of recent patent applications aimed at the introduction of novel eco-friendly trivalent chromium electrolytes in near future industrial ECCS processes [18–20].

## 2. Experimental

### 2.1. Electrolytes

Six different electrolyte compositions were prepared from a basic chromium(III) sulphate salt ($(CrOHSO_4)_2{\cdot}Na_2SO_4{\cdot}H_2O$) with trade name Trisurfin® supplied by Soda Sanayii A.Ş., sodium sulphate and sodium formate (Table 1). All electrolytes contain 900 mM $Na_2SO_4$ as supporting salt. Electrolyte F also contains sodium formate and electrolytes C also contain the chromium salt with an increasing formate/Cr(III) molar ratio.

All electrolytes were adjusted to pH 2.8 at 25 °C by adding sulphuric acid. The pH choice is based on an optimisation study (not part of this study). Mixed chromium metal-carbide-oxide coatings with the desired composition and appearance are obtained from the electrolyte at a pH between 2.6 and 3.0 with a high deposition rate and current efficiency.

### 2.2. Cyclic voltammetry measurements

The working electrode was either a mirror polished platinum Rotating Disk Electrode (RDE) tip from Pine Instrument Company or a titanium electrode disk with a catalytic mixed metal oxide (MMO) coating comprising iridium oxide ($IrO_2$) and tantalum oxide ($Ta_2O_5$) supplied by Magneto Special Anodes B.V., fitted in a ChangeDisk RDE tip from Pine Instrument Company. The outer diameter of the disks was 5 mm.

Prior to the measurements, the Pt RDE was cleaned in a 0.1 M $H_2SO_4$ 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 PGSTAT302 N potentiostat. A Saturated Calomel Electrode (SCE) was used as reference electrode and 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.

**Table 1**
Electrolyte compositions.

| code | $Na_2SO_4$ (mM) | $CrOHSO_4$ (mM) | HCOONa (mM) | formate/Cr(III) (molar ratio) |
|---|---|---|---|---|
| A | 900 | – | – | – |
| F | 900 | – | 200 | – |
| C-0% | 900 | 400 | – | 0% |
| C-50% | 900 | 400 | 200 | 50% |
| C-100% | 900 | 400 | 400 | 100% |
| C-150% | 900 | 400 | 600 | 150% |

### 2.3. On-Line Electrochemical Mass Spectrometry (OLEMS) measurements

On-line Electrochemical Mass Spectrometry (OLEMS) was used to detect gaseous products of the reactions [21]. The products were collected with a small hydrophobic tip that was positioned close (about 10 μm) to the working electrode with the aid of a camera. The tip was constructed as a porous Teflon® (PTFE) cylinder with a diameter of 0.5 mm and an average pore size of 10–14 μm in a Kel-F® (PCTFE) holder. The tip is connected to a mass spectrometer with a PEEK capillary. Before use the tip was rinsed thoroughly with Millipore water. A Secondary Electron Multiplier (SEM) voltage of 2400 V was used for detection in a Balzers Quadrupole mass spectrometer. The products were measured while changing the potential of the electrode from −0.4 V vs. SCE to +1.4 V vs. SCE and back at 1 mV $s^{-1}$.

The OLEMS measurements were performed with a stationary Pt electrode at 20 °C.

### 2.4. Long-term galvanostatic experiments

For trace analysis, a significant amount of Cr(VI) must be formed above the detection limit. For this purpose, long-term galvanostatic experiments were carried out at a fixed current of 92.0 mA for 3600 s using a DIGISTANT® 6425 T precision current source from Burster Präzisionsmesstechnik. Because the fine-meshed circular platinum gauze used as counter electrode has a very large surface area compared to the working electrode, the cathodic current was much lower than the threshold value required for applying a mixed chromium metal-carbide-oxide deposit [5]. So, virtually only hydrogen gas is formed at the counter electrode during the electrolysis experiments.

### 2.5. Trace analysis of Cr(VI)

The Cr(VI) concentration in the Cr(III) electrolyte was analysed by means of Differential Pulse Polarography (DPP) using a Metrohm 663 VA Stand polarographic analysis system fitted with a Multi Mode Electrode (MME). The average weight of a mercury droplet was 0.219 mg corresponding to a surface area of 0.309 $mm^2$ assuming a perfect spherical shape.

The initial potential was +0.1 V, the end potential −0.3 V and the step potential 0.05 V vs. an Ag/AgCl/KCl (sat'd) reference electrode.

First 50.0 ml of a 0.1 M di-ammonium L(+)-tartrate solution adjusted with ammonia to pH 9.0 was added to the measuring vessel. Then 1.0 ml of the electrolyte was added with a micropipette. The solution was purged for with $N_2$ to remove $O_2$ from the solution.

To validate the analysis method and for calibration purpose 100.0 μl of a 1.0 mM $K_2Cr_2O_7$ solution was added stepwise to the solution.

The DPP polarograms are shown in Fig. 1. The small anodic shift of the peak potential is caused by a gradual decrease of the pH from 9.0 to 7.9 due to evaporation of ammonia. The excellent correlation between the concentration of Cr(VI) and the peak current is clearly demonstrated in the inset in Fig. 1.

## 3. Results and discussion

### 3.1. Pt: electrolyte A ($Na_2SO_4$)

CV measurements were executed in the supporting electrolyte A (900 mM $Na_2SO_4$) and show the expected positions of $H_2$ evolution, $O_2$ evolution and reduction, and PtO formation and reduction.

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