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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 voltammogrammetric 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.

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 (IrO_2) and tantalum oxide (Ta_2O_5) [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 CO_2 is completely suppressed when basic chromium sulphate ($(CrOHSO_4)_2 \times Na_2SO_4$) 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 CO_2 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 SO_2 [16]:

$$Na_2Cr_2O_7 + H_2O + 3SO_2 \rightarrow (CrOHSO_4)_2 \times Na_2SO_4$$

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 SO_2 will result in the formation of sulphurous acid (H_2SO_3), which may in turn form sulphite anions:

$$SO_2 + H_2O \rightarrow H_2SO_3 \leftrightarrow 2H^+ + SO_3^{2-}$$

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 ($(CrOHSO_4)_2 \cdot Na_2SO_4 \cdot H_2O$) with trade name Trisurfin® supplied by Soda Sanayii A.Ş.

All electrolytes contain 900 mM Na_2SO_4 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 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 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 $m^3 h^{-1}$ 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 (IrO_2) and tantalum oxide (Ta_2O_5) 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 CO_2 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 CO_2(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

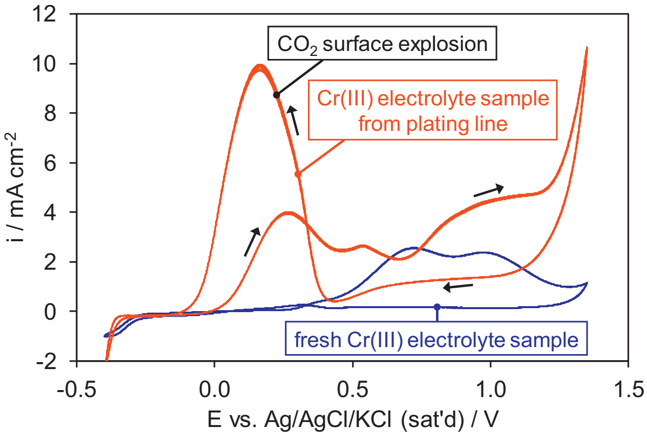

Fig. 1. Cyclic voltammograms of a fresh Cr(III) electrolyte sample (blue curve) and a Cr(III) sample from a plating line (red curve) with similar composition (900 mM Na_2SO_4 + 400 mM $CrOHSO_4$ + 600 mM HCOONa). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

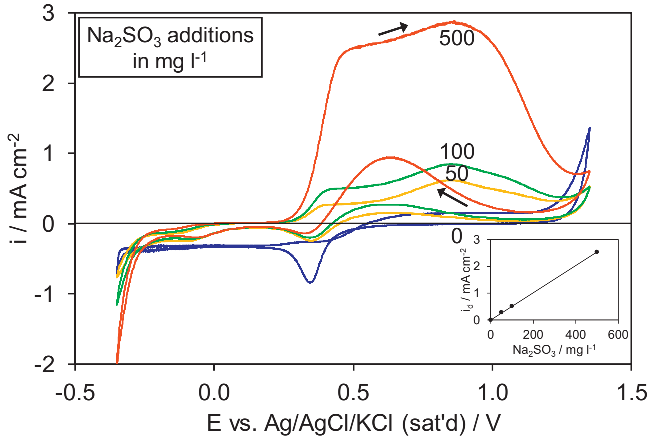

Fig. 2. Cyclic voltammograms in a 900 mM Na_2SO_4 electrolyte with various Na_2SO_3 additions (blue curve: 0, orange curve: 50, green curve: 100, red curve 500 mg l^{-1} Na_2SO_3). Inset: diffusion-limited current density vs. Na_2SO_3 concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

negative sweep (potentials where platinum oxides are not yet reduced) may be an indication of the latter.

The addition of sulphite blocks the oxygen reduction; the current becomes zero between 0 and 0.2 V. Below 0 V a reductive current is measured with an additional wave at −0.2 V.

The entire CV shows that sulphite adsorbs strongly on platinum, and is readily oxidised.

Cycling between −0.2 V resp. −0.35 V shows a strong effect on the subsequent oxidation current of sulphite (Fig. 3). We infer that sulphite can form intermediates that poison subsequent oxidation. These intermediates are reduced below −0.2 V, activating the surface for rapid oxidation of sulphite.

The cyclic voltammogram and the effect of increased concentration are in line with literature [17,18], in which the strongly adsorbed intermediate was assumed to be pure sulphur.

3.3. Effect of sulphite on formic acid oxidation

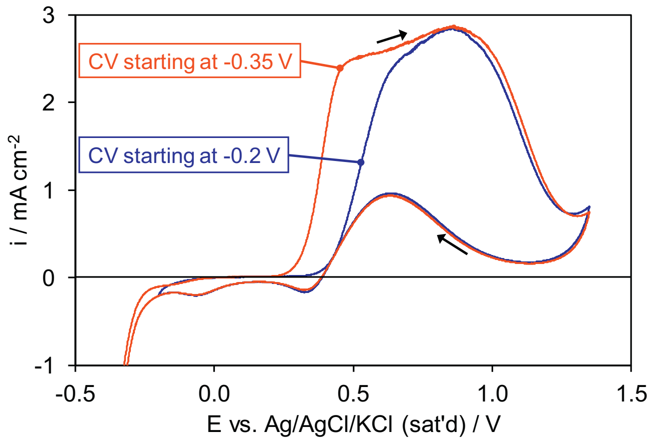

Fig. 3. Cyclic voltammograms in a 900 mM Na2SO4 electrolyte with 500 mg l^{-1} Na_2SO_3 and a lower vertex potential of −0.2 (blue curve) and −0.35 V (red curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

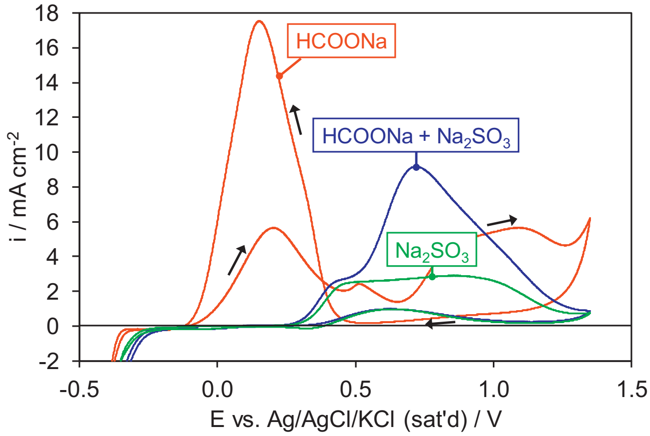

Fig. 4. Cyclic voltammograms in electrolytes with the following compositions: 900 mM Na_2SO_4 + 200 mM HCOONa (red curve), 900 mM Na_2SO_4 + 200 mM HCOONa +500 mg l^{-1} Na_2SO_3 (blue curve) and 900 mM Na_2SO_4 + 500 mg l^{-1} Na_2SO_3 (green curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The CV of formic acid on platinum (Fig. 4: red curve) has been discussed in detail in our previous publication and references therein [15]. The main characteristic feature is the high oxidation current at +0.2 V. This ‘surface explosion’ is the result of the combination of three conditions: 1. a relatively high overpotential for formic acid oxidation, 2. the availability of metallic platinum and 3. the absence of CO poisoning of the surface.

When sulphite is added (blue curve), the oxidation of formic acid on metallic platinum is completely inhibited: the current is zero between −0.2 and + 0.4 V. This shows that sulphite is adsorbed strongly on platinum, much stronger than formic acid.

An oxidative current is observed above 0.4 V at the same potential where sulphite itself is oxidised: the blue curve (with formic acid) is higher than the green curve (without formic acid). The additional current is most likely related to formic acid oxidation, which is only possible after sulphite is oxidised and removed from the surface.

3.4. Addition of basic chromium salt

The addition of Cr(III) to a sulphite containing electrolyte is

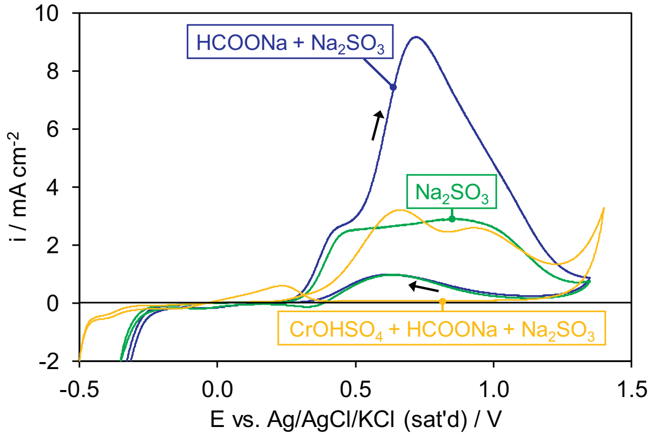

Fig. 5. Cyclic voltammograms in electrolytes with the following compositions: 900 mM Na_2SO_4 + 200 mM HCOONa +500 mg l^{-1} Na_2SO_3 (blue curve), 900 mM Na_2SO_4 + 500 mg l^{-1} Na_2SO_3 (green curve) and 900 mM Na_2SO_4 + 400 mM $CrOHSO_4$ + 600 mM HCOONa +500 mg l^{-1} Na_2SO_3 (orange curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

shown in Fig. 5. The main observation is the blocking of formic acid oxidation on metallic platinum, in line with the previous curves. The oxidation of sulphite between 0.3 and 0.5 V in the positive sweep is slightly reduced, as well as the reductive current between −0.3 and −0.5 V. Both are an indication that some species is adsorbed at the surface, which is not reduced at negative potentials (Fig. 3 showed that adsorbed sulphite itself is reduced at those potentials).

An oxidative current in two waves is seen between 0.5 and 1.0 V: OLEMS measurements have demonstrated that the second wave is mainly CO_2 formation (Fig. 6).

Fig. 6 was recorded with a fresh electrolyte. Recording an OLEMS measurement of a used electrolyte was not performed because the CV of a used electrolyte (Fig. 1: red curve) is identical to the CV of formic acid (Fig. 4: red curve). Thus, the only reactions occurring in a used electrolyte are those of formic acid.

A final difference is an increase in oxidative current above 1.3 V, which does not occur in the absence of Cr(III). It is also demonstrated that Cr(III) can be oxidised to Cr(VI) on platinum electrodes under steady state current. We therefore assign this current, at least in part, to the oxidation of Cr(III) to Cr(VI).

Ideally a graph of Cr(III) without the sulphite contamination would be recorded. Unfortunately, such salts are not available: they are either poorly soluble or have other pollutants, like organic acids.

Our previous publication stated that the second peak of the cyclic voltammogram (at 0.9 V) is linked purely to the formation of CO_2, whereas the first peak is in part due to a different adsorption process. At the time we assumed it was the oxidative adsorption of the Cr(III)-formate complex. However, our new results indicate that this current is rather linked to the oxidation of sulphite at the electrode, which blocks the oxidation for formic acid.

3.5. *Removal of sulphite from Cr(III) electrolyte by electrolysis*

3.5.1. *Electrolysis experiments in flow channel cell*

Because we noticed that the CV of a fresh Cr(III) electrolyte sample is very different from the CV of a Cr(III) electrolyte sample from a plating line after several hours of operation, as shown in Fig. 1, a well-defined electrolysis experiment was set-up in a flow channel cell.

The Cr(III) plating process is assumed to be based on a fast, stepwise deprotonation of the water ligands in the Cr(III)-complex ion induced by a surface pH increase as a result of the hydrogen evolution reaction [3]. This mechanism leads to the existence of a so-called 'regime I', wherein no chromium is deposited even though an electrical current is applied. In regime I, besides hydrogen evolution, the following acid-base reaction takes place [3]:

$$[Cr(HCOO)(H_2O)_5]^{2+} + OH^- \rightarrow [Cr(HCOO)(OH)(H_2O)_4]^+ + H_2O$$

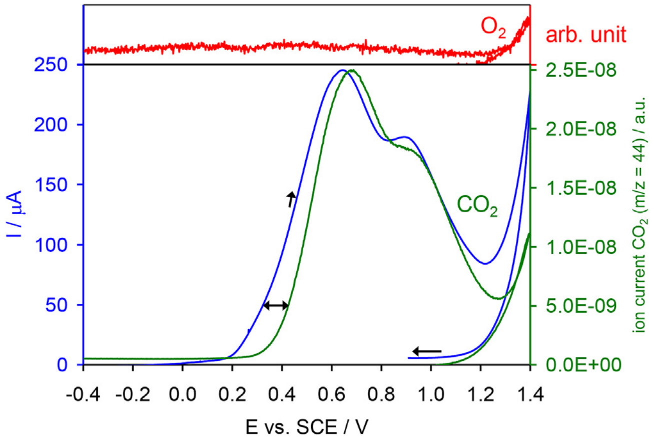

Fig. 6. OLEMS measurement of CO_2 and O_2 in Cr(III)-formate electrolyte (900 mM Na_2SO_4 + 400 mM $CrOHSO_4$ + 600 mM HCOONa) for a stationary Pt electrode at a scan rate of 1 mV s^{-1} obtained from ref. 15.

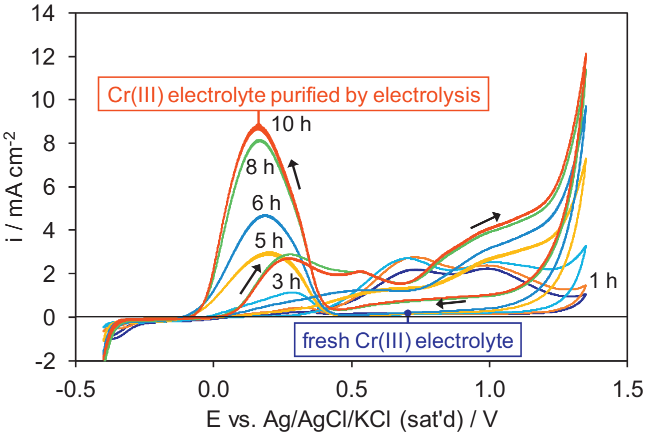

Fig. 7. Cyclic voltammograms of electrolyte samples from flow channel cell.

A current density of 10 A dm^{-2} within regime I was chosen for purification of the electrolyte. Each hour 100 ml electrolyte was sampled for recording a CV. In Fig. 7, the CVs of the electrolyte samples are plotted. Clearly, the CV gradually transforms to an identical shape as the CV of a Cr(III) electrolyte sample from a plating line after several hours of operation plotted in Fig. 1. This is attributed to the removal of sulphite from the electrolyte.

3.5.2. *Electrolysis experiments in two-compartment cell*

To elucidate whether purification of the electrolyte proceeds via reduction or oxidation of sulphite, an electrolysis experiment was executed in a two-compartment cell.

A current density of 10 A dm^{-2} was applied for 4 h. During electrolysis, the pH of the catholyte had increased from 2.8 to 4.7 due to hydrogen evolution ($4H^+ + 4e^- \rightarrow 2H_2$) and conversely the pH of the anolyte had decreased to 2.3 due to oxygen evolution ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$).

In Fig. 8, the CVs of the catholyte and anolyte are plotted.

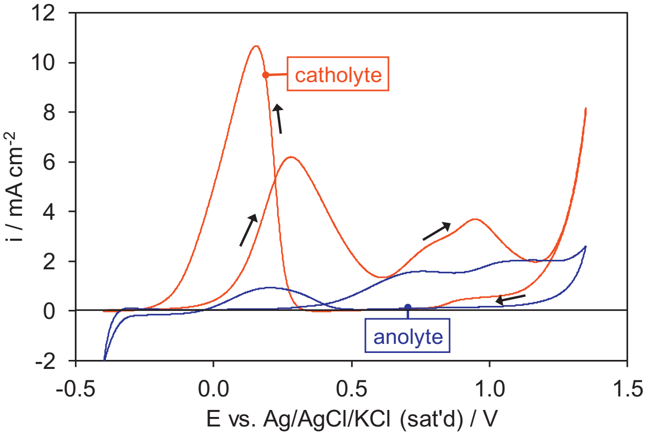

Fig. 8. Cyclic voltammograms of catholyte (red curve) and anolyte (blue curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

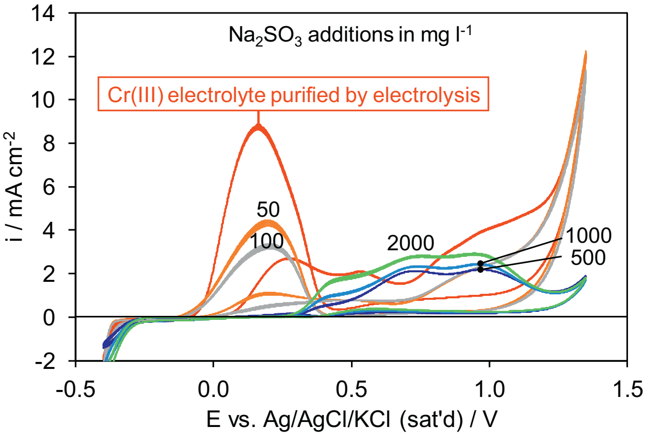

Fig. 9. Cyclic voltammograms of purified electrolyte with Na_2SO_3 additions as indicated.

Unmistakably, the $CO_2(g)$ surface explosion peak arises in the CV of the catholyte, which proofs that sulphite is reduced to hydrogen sulphide:

$$SO_3^{2-} + 8H^+ + 6e^- \rightarrow H_2S + 3H_2O$$

This experiment also explains the characteristic smell of H_2S that is only experienced during the first hours after a fresh Cr(III) electrolyte is put into operation.

3.6. Adding sulphite to purified Cr(III) electrolyte

As a final confirmation of the importance of sulphite, sodium sulphite was intentionally added stepwise to purified electrolyte (Fig. 9). The CO_2 surface explosion peak is completely suppressed after adding 500 mg l^{-1} Na_2SO_3 to the electrolyte. The CV of purified electrolyte with 500 mg l^{-1} Na_2SO_3 added is almost identical to the CV of fresh electrolyte (Fig. 10).

4. Discussion and conclusions

The oxidation of sulphite clearly occurs at high rates on metallic platinum, like the oxidation of formic acid. When the two species are mixed, the features of sulphite dominate the cyclic voltammogram up to 0.6 V, which can be attributed to its stronger adsorption. It is therefore logical to attribute the first peak of the cyclic voltammogram in the presence of Cr(III) + formic acid + sulphite to the oxidation of adsorbed sulphite.

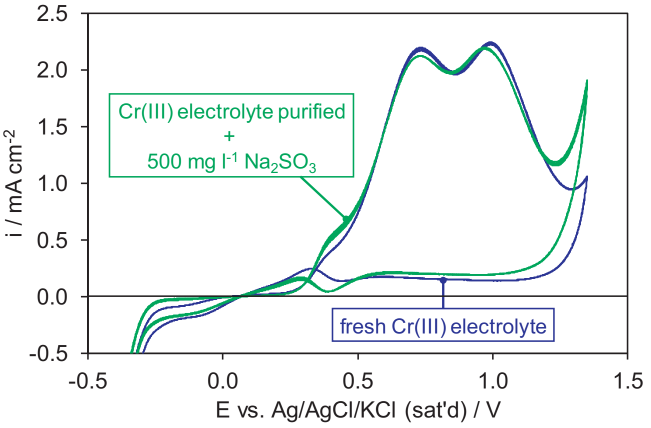

Fig. 10. Cyclic voltammograms of fresh electrolyte and purified electrolyte with 500 mg l^{-1} Na_2SO_3 added.

Above 0.6 V the cyclic voltammogram assumes the features of formic acid oxidation: the steady-state oxidation rate is replaced by a peak associated with CO_2 formation. This CO_2 is indeed observed in the OLEMS measurement as the second peak.

Finally, if the sulphite is removed by electrolysis, the cyclic voltammogram adopts the characteristic shape of that of formic acid.

These observations falsify the assumption in our previous publication that the Cr(III)-formic acid complex adsorbs strongly at the platinum electrode. The hindrance of chromium deposition on a steel electrode in the presence of sulphite can be explained by assuming that preferential adsorption of sulphite also occurs on steel. Several mechanisms are possible: adsorbed sulphite might block the adsorption of the Cr(III)-complex and/or interfere with the pH-gradient near the electrode (a requirement for chromium deposition that takes place via acid/base reactions [3]). Strong specific adsorption of sulphite to the steel electrode is in line with the high current efficiency of its removal: without specific adsorption it would be expected that transport of sulphite ions to the electrode would be limiting at low concentrations, which is in contrast to what is measured.

Purification of a fresh 400 mM Cr(III) electrolyte in the flow cell experiment (see § 3.5.1) was completed after 10 h. Assuming a pollution of 500 mg l^{-1} Na_2SO_3 and a six-electron reduction reaction, the current efficiency for sulphite removal is about 21%. This high current efficiency is in line with strong specific adsorption of sulphite onto the cathode. A much lower number would be expected without specific adsorption as the probability of the sulphite ion interacting with the electrode decreases with concentration.

500 mg l^{-1} Na_2SO_3 corresponds to 4 mM vs. 400 mM Cr(III), which is a pollution of 1 mol-% of the chromium salt. This number might seem high, but is understandable when realising the chemical producers are very keen on avoiding trace amounts of Cr(VI) in their chemicals.

Even though the Cr(III) complex adsorbs weakly, the oxidation of the Cr(III) ion at potentials above 1.2 V has been demonstrated, both in the presence and absence of sulphite. The formation of Cr(VI) under steady state oxidative currents has been proven earlier. Both features are absent on iridium-based mixed metal oxide electrodes. The exact reason for this difference in catalytic activity is unexplained yet.

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