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Original scientific paper

On the suppression of cathodic hypochlorite reduction by electrolyte additions of molybdate and chromate ions

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Abstract

The goal of this study was to gain a better understanding of the feasibility of replacing Cr(VI) in the chlorate process by Mo(VI), focusing on the cathode reaction selectivity for hydrogen evolution on steel and titanium in a hypochlorite containing electrolyte. To evaluate the ability of Cr(VI) and Mo(VI) additions to hinder hypochlorite reduction, potential sweep experiments on rotating disc electrodes and cathodic current efficiency (CE) measurements on stationary electrodes were performed. Formed electrode films were investigated with scanning electron microscopy and energy-dispersive X-ray spectroscopy. Cathodic hypochlorite reduction is hindered by the Mo-containing films formed on the cathode surface after Mo(VI) addition to the electrolyte, but much less efficient compared to Cr(VI) addition. Very low levels of Cr(VI), in the μM range, can efficiently suppress hypochlorite reduction on polished titanium and steel. Phosphate does not negatively influence the CE in the presence of Cr(VI) or Mo(VI) but the Mo-containing cathode films become thinner if the electrolyte during the film build-up also contains phosphate. For a RuO_2-TiO_2 anode polarized in electrolyte with 40 mM Mo(VI), the anode potential increased and increased molybdenum levels were detected on the electrode surface.

Keywords

Current efficiency; hydrogen evolution; in-situ additives; cathode; electrolysis; EDS; SEM; potential sweeps; galvanostatic polarization

Introduction

Sodium chlorate is industrially produced from sodium chloride in an electrolytic process according to reaction 1 below.

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2 \qquad (1)$$

Chlorine is produced on the anode and forms hypochlorite (here defined as ClO^- + $ClOH$) (reactions 2-4) [1], and chlorate is formed in a chemical reaction (reaction 5) that shows an optimal reaction rate at pH 6-7. To prevent that the intermediate hypochlorite and the product chlorate are reduced on the cathode (reactions 6, 7 and 8) hexavalent chromium, Cr(VI), is added to the electrolyte. The hexavalent chromium is reduced on the cathode surface to a film of chromium (III)hydroxide [2]. The $Cr(OH)_3$-film formed has been shown to be very thin and efficient at inhibiting the reduction of hypochlorite, chlorate [3], oxygen and ferricyanide [2].

$$2Cl^- \leftrightarrow Cl_2 + 2e^- \qquad (2)$$

$$Cl_2 + H_2O \leftrightarrow HClO + Cl^- + H^+ \qquad (3)$$

$$HClO \leftrightarrow ClO^- + H^+ \qquad (4)$$

$$2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \qquad (5)$$

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \qquad (6)$$

$$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad (7)$$

$$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^- \qquad (8)$$

Unfortunately Cr(VI) is toxic and carcinogenic, which motivates investigations of possible alternatives.

Molybdenum is in the same group as chromium in the periodic table and the two elements have similarities. Molybdate (MoO_4^{2-}) is opposed to chromate not toxic and is used as an environmentally friendly alternative to Cr(VI) in corrosion applications [4]. Mo-containing cathode films are formed during electrolysis of an electrolyte with Mo(VI), and these films can hinder the cathodic reduction of oxygen on copper [5]. This inhibition was shown to be efficient in electrolytes of neutral pH, where films of MoO_2 are stable. Mo(VI) also buffers in a pH region close to that of Cr(VI) [6] and can activate the desired cathode reaction of hydrogen evolution [6,[7]. Not surprisingly Mo(VI) has been considered as a possible alternative to Cr(VI) in the chlorate process [6],[8]. A potential problem observed with Mo(VI) electrolyte additions to chlorate electrolyte is an increased oxygen level in the hydrogen cell gas [6], as this would affect the overall current efficiency (CE) for chlorate production as well as being a safety risk if the oxygen/hydrogen mixture reaches an explosive composition. Other results showed though that at low Mo(VI) concentrations (typically < 1 mM Mo(VI) compared to 39 mM Mo(VI) in [6]) no increased oxygen levels were reached and still the hydrogen evolution reaction on MAXTHAL® 312 (Ti_3SiC_2) was substantially activated [8], by the Mo(VI) addition. Whether the increased oxygen levels related to homogeneous reaction in the electrolyte or to anode reactions is not clear, and no measurements of the anode potential were made in [6] or [8].

At low levels of Mo(VI) or Cr(VI) an additional buffer may be needed to stabilize the electrolyte pH in the chlorate process at 6-7. Phosphate is a possible buffer alternative, which may also form cathode films that can affect the CE [9] and thus the CE in electrolytes containing combinations of Mo(VI), Cr(VI) and phosphate are of interest.

The goal of this study is to gain a better understanding of the feasibility of replacing Cr(VI) in the chlorate process by Mo(VI), focusing on the cathode reaction selectivity in the presence of a Mo-containing film. Reaction 6 or 7, the reduction of hypochlorite, was chosen as an indicator of the ability of different films to increase the CE for hydrogen evolution. Experiments with Cr(VI) additions to the electrolyte were made to compare the effects of Mo(VI) and Cr(VI). Cathodes of low carbon steel and titanium were used, as these are the most common cathode materials in chlorate electrolysis today. Both rotating disc electrodes (RDE) and stationary electrodes were used. The possibility of effects on the anode reactions of electrolyte additives were studied on a dimensionally stable anode (DSA)-type RDE.

Experimental

Water purified in a Millipore Direct-Q system was used in the preparation of all electrolytes, and to rinse the electrodes prior to experiments. Sodium hydroxide, sodium chloride, hydrochloric acid, sodium molybdate dihydrate, sodium dihydrogen phosphate all from Merck and of Pro Analysi grade; sodium hypochlorite solution 0.5 M in 0.1 M NaOH from VWR BDH Prolabo. In the text the term “hypochlorite” refers to the sum of [ClO^-] and [HClO]. If not stated otherwise, the given hypochlorite concentration was the initial concentration. The terms “phosphate concentration” or “total phosphate concentration” here refers to the sum of phosphate species $[PO_4^{3-}]_{tot}=[H_3PO_4]+ +[H_2PO_4^-]+ [HPO_4^{2-}]+ [PO_4^{3-}]$.

For potential sweeps and polarization experiments RDEs were used and the measurements were performed using a PAR 273A potentiostat and an electrode rotator Model 616 from Pine Instrument Company. The Fe-RDE (5 mm diameter) and Ti-RDE (diameter 4 mm) were shielded by Teflon sheaths, polished by grit 4000 SiC grinding paper and rinsed in water before all experiments. The Fe-RDE was prior to the measurements corroded by immersion at OCP for 3 min with no rotation, in an electrolyte containing 5.2 M $NaClO_3$, 1.9 M NaCl and 10 mM NaClO, pH 6.5 at 70°C. The potential sweep and polarization experiments were performed in a jacketed glass cell with 200 ml electrolyte. The temperature was controlled by a water bath and the electrolyte was purged with nitrogen for at least 15 min prior to and during the experiments. The reference electrodes connected to the electrolyte by an ion bridge filled with 5 M NaCl and a Luggin capillary. As the counter electrode a platinum grid was used.

For investigation of effects on the anode reactions polarization experiments were performed on a DSA-type anode. The anode was produced by spin-coating to produce a well-defined and relatively smooth coating of $Ti_{0.7}Ru_{0.3}O_2$. A solution of 5.351 g $RuCl_3 \cdot nH_2O$ (Ru content 35.51 % by mass) and 14.929 g Ti(IV)n-butoxide in n-propanol to a final volume of 50 ml was prepared. The solution was thoroughly stirred for several days. A disc of commercially pure titanium with smooth surface and a diameter of 59 mm was pickled in an aqueous solution of 27 ml concentrated HF per liter and 71 ml concentrated HNO_3 per liter for two min at room temperature. The disc was placed in a spin coater (Electronic Micro Systems), an amount of solution was applied to the surface of the disc, and the solution was evenly distributed by spinning at 550 min^{-1}. The disc was then dried at 80 °C for 10 min and calcined at 470 °C for 10 min. Three layers of coating were applied the same way. The final layer was dried for 40 min and calcined for one hour. The mass difference between the bare disc and the final sample was 0.0883 g corresponding to a Ru loading of 10.2 g m^{-2}. To make DSA-RDEs, small discs (diameter 11.3 mm) were punched from the larger disc and put into titanium holders. Exposed titanium was shielded by silicon tubing and epoxy. For the anodic polarization experiments the electrodes were pre-polarized for 30 min at 3 kA m^{-2} in a separate

2 M NaCl electrolyte at 70 °C. The recorded potentials were IR-corrected using a current interrupt technique [10].

Measurements of the CE for hydrogen evolution were performed in a divided cell [11] separated by a Gore Select ion-exchange membrane. The cell was immersed in a water bath for temperature control and a magnetic stirrer, set at the same level for all experiments, was used for the cathode compartment. The length of time needed to produce a given volumes of hydrogen gas (between 5 and 20 ml) were recorded. The CE was determined as by calculation from a calibration curve where hydrogen was evolved on a Pt-wire in Na_2SO_4 solution under the assumption of 100 % CE for hydrogen evolution. For the CE measurements stationary electrodes of titanium and low carbon steel were used. The electrodes were polished with grit 4000 SiC grinding paper and rinsed in water before all experiments. For CE measurements in neutral and alkaline electrolyte the hypochlorite level was measured using arsenite titration. The arsenite titration was performed with 5 ml electrolyte diluted by 200 ml water and pH adjusted to neutral pH. Mo(VI) was found to interfere with the titration, giving unreasonable high “hypochlorite levels”. Therefore hypochlorite levels in the electrolyte were only measured in experiments where no Mo(VI) had been added to the electrolyte. The hypochlorite concentration typically decreased from 80 to 40 mM after 20 min of electrolysis at -3 kA m^{-2}, and the corresponding pH increased from 6.5 to 9-11.

X-Ray Fluorescence (XRF) measurements were performed using a Niton XLT898 with an accelerator voltage of 35 kV and a silver anode. Two different instruments for Scanning Electron Microscopy (SEM) were used; a Zeiss EvO 50 SEM with EDS for the elemental analyses and a Hitachi S-4800 field emission SEM for the micrographs presented.

Results and discussion

Current efficiency for hydrogen evolution in the presence of molybdate

Potential sweep experiments on a Ti-RDE with and without additions of Mo(VI) and hypochlorite to the electrolyte are shown in Figure 1. The sweeps were made in anodic direction after 5 min of pre-polarization at -1.5 V *vs.* Ag/AgCl, which enabled the formation of Mo-containing films on the cathode whenever the electrolyte contained Mo(VI). In the presence of 15 mM hypochlorite, the dotted line, a cathodic limiting current for hypochlorite reduction of about 350 A m^{-2} can be seen. This limiting current was suppressed by the addition of Mo(VI), and the higher the Mo(VI) concentration the more efficient the hindering effect – see curves with addition of 1, 10 and 100 mM Mo(VI), respectively. From the Levich equation and data for viscosity and diffusivity from Byrne et al. [12] a limiting current density for hypochlorite reduction of 340 A m^{-2} was calculated, which agrees well with the experimental result.

Looking at the cathodic end of the graph an activation of hydrogen evolution about 300 mV is seen for the cases of 1 and 10 mM Mo(VI). As high Mo(VI) level as 100 mM did not give a similar decrease in overpotential, likely caused by resistive properties of the Mo(VI) film formed [7].

In Figure 2 potential sweeps on slightly corroded iron are shown, and the electrode had been pre-polarized as above. Again a limiting current for hypochlorite reduction is visible at -300 to -400 A m^{-2}, and addition of 100 mM Mo(VI) only partly suppressed this current. A comparison with the result in Figure 1 indicates that it is easier to form a hindering film on a titanium substrate than on corroded iron. The high currents appearing at potentials > -0.6 V *vs*. Ag/AgCl in the Mo(VI) free case likely relate to oxidation of the iron electrode, which is hindered by the presence of a molybdenum containing film. Similar as in the case of titanium cathodes (Figure 1) the addition of as high concentration as 100 mM Mo(VI) was less effective at activating the HER than lower Mo(VI) concentration.

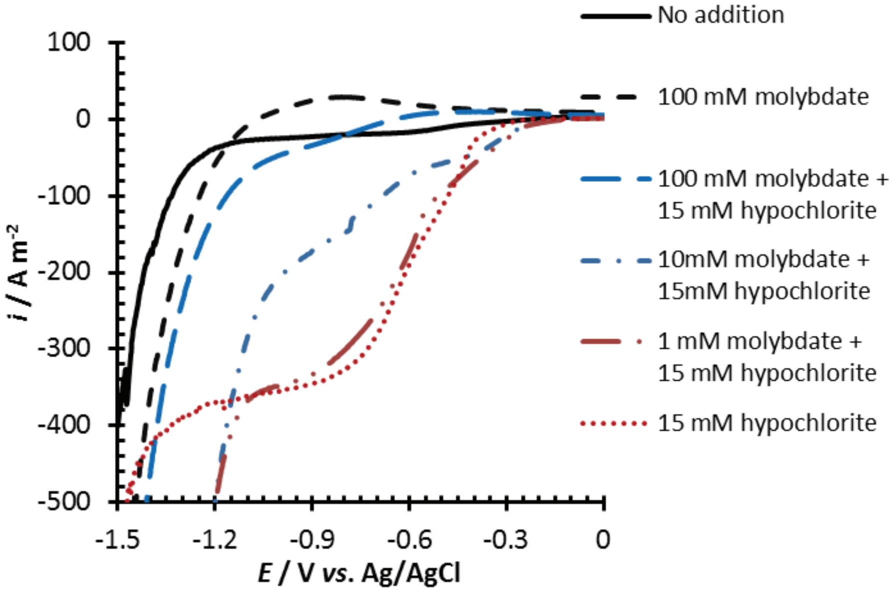

Figure 1. *Potential sweeps from -1.5 V to 0 V* vs. *Ag/AgCl at a sweep rate of 50 mV/s in 5 M NaCl, 70 °C, pH 6.5 with a Ti-RDE at a rotation rate of 3000 rpm. Pre-polarization at -1.5 V* vs. *Ag/AgCl for 5 min.*

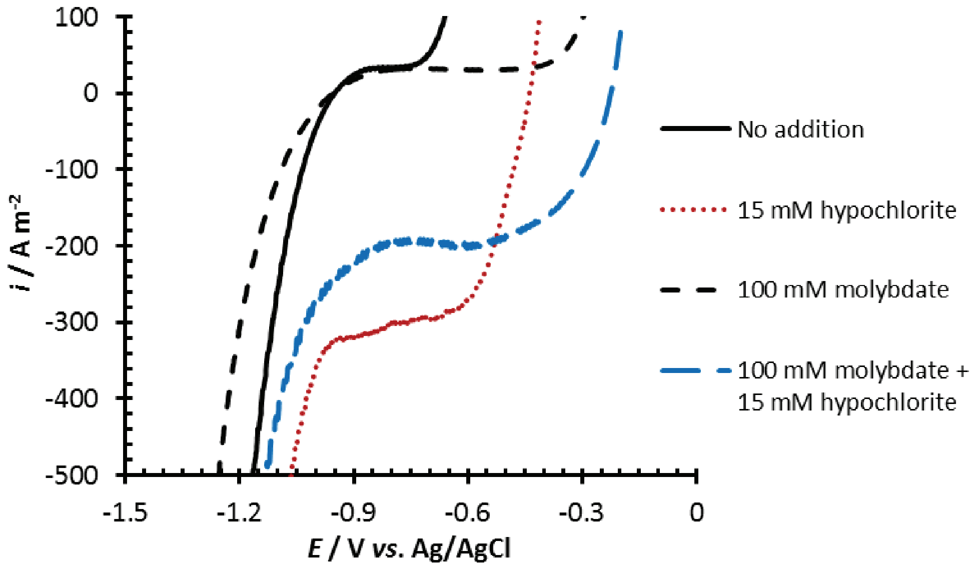

Figure 2. *Potential sweeps from -1.5 V to 0 V* vs. *Ag/AgCl at a sweep rate of 50 mV s^{-1} in 5 M NaCl, pH 6.5, 70 °C with a corroded Fe-RDE at a rotation rate of 3000 rpm. Pre-polarization at -1.5 V* vs. *Ag/AgCl for 5 min.*

Measurements of the CE for hydrogen evolution were made to evaluate how hypochlorite reduction as a side reaction could be suppressed at an industrially relevant current density of -3 kA m^{-2}, which corresponds to a potential region where hydrogen evolution prevails. In pH neutral electrolyte the CE on titanium was around 80 % in the presence of 80 mM hypochlorite (Figure 3). When adding 80 mM Mo(VI) the CE increased to 91-94 %. Thus, similar as shown in the potential sweeps (Figure 1), addition of Mo(VI) to a pH neutral electrolyte can hinder hypochlorite reduction on a titanium cathode. In alkaline pH the CE was lower (Figure 3), and some possible explanations for this are (i) a higher and more stable hypochlorite concentration of 80 mM,

(ii) a better mass transport of hypochlorite to the cathode surface due to a lower viscosity of the sodium hydroxide electrolyte compared to 5 M NaCl and (iii) at alkaline pH hypochlorite is present as the ion ClO^-, which is possibly more easily reduced compared to HClO [12]. The CE was still low after addition of Mo(VI), 55-60%, although there seems to be some minor hindrance of hypochlorite reduction.

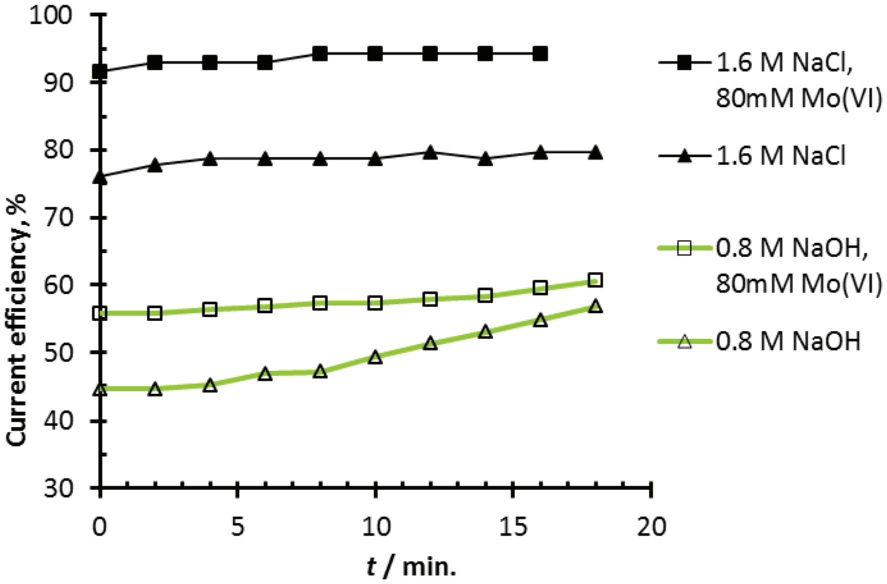

Figure 3. *Current efficiency measurements for hydrogen evolution on stationary titanium electrode polarized at -3 kA m^{-2}, 70 °C. Initially: [hypochlorite] ≈80 mM, pH 6.5 respectively pH ≈13*

The relatively high concentration of 80 mM Mo(VI) was chosen to see an immediate response of the addition, though at a realistic process a lower concentration is probably needed to avoid high cathode overpotentials and high oxygen levels in the off gas [8]. An experiment with 4 mM Mo(VI) was made, showing that such low concentrations are required over 30 min to give any effect at all on the CE, see Figure 4. The effect would probably be increased if the experiment was continued, giving the Mo-containing cathode film a longer time to build up.

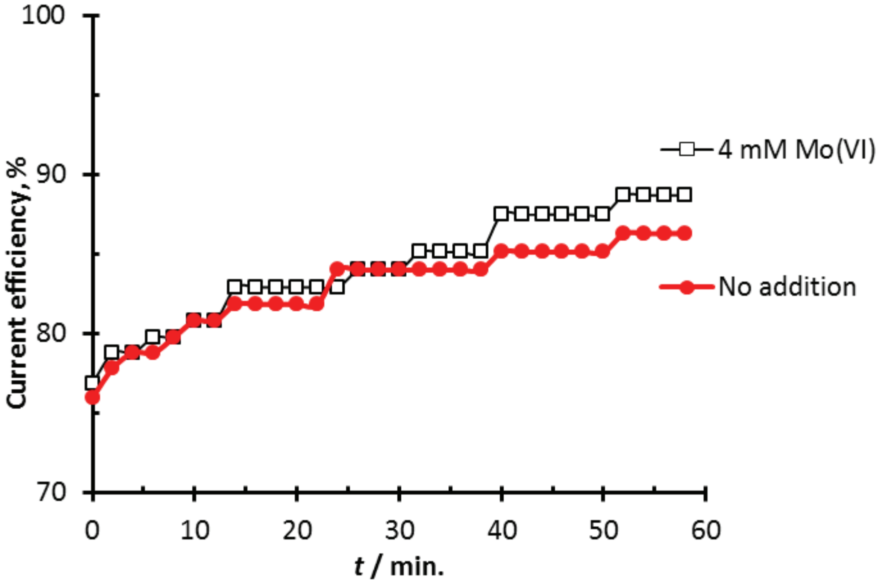

Figure 4. *Current efficiency measurements for hydrogen evolution on stationary titanium electrode polarized at -3 kA m^{-2} 1.6 M NaCl, 70 °C. Initially: [hypochlorite] ≈80 mM, pH 6.5*

As mentioned in the introduction the addition of Cr(VI) to industrial chlorate electrolyte has several functions, one of which is to buffer the electrolyte pH. If replacing Cr(VI) by low levels of Mo(VI), or if lowering considerably the levels of Cr(VI), an additional buffer such as phosphate would be needed. Measurements of the CE on titanium in the presence of phosphate were made to see if possible phosphate films would interfere with the Mo-containing cathode films. As seen in Figure 5 the addition of phosphate had no negative effect on the CE. In contrast, it showed a small positive effect. It has earlier been found that molybdate and phosphate have a synergistic effect on preventing corrosion of an Mg alloy [13].

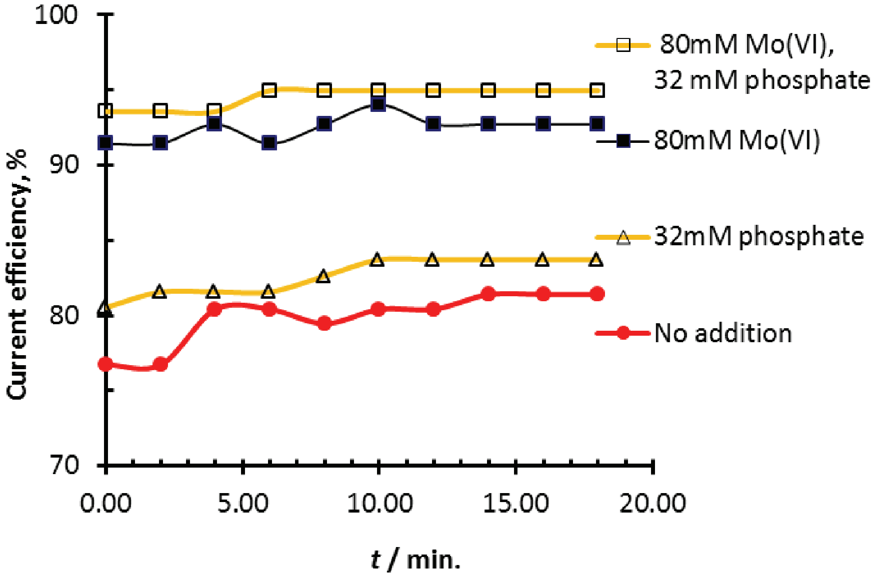

Figure 5. *Current efficiency measurements for hydrogen evolution on a stationary titanium electrode at -3 kA m^{-2} in 1.6 M NaCl, 70 °C. Initially: [hypochlorite]$\approx$80 mM, pH 6.5*

Results from measurements of CE on a steel electrode can be seen in Figure 6. Lower CE-values were obtained on steel compared to on titanium, which is consistent with our results from the potential sweeps in Figures 1 and 2. Furthermore, also on steel the phosphate additions had no negative effects on the CE, but could possibly increase it a little. The CE values in Figure 6 are relatively low in the beginning of the experiments, and then gradually increase – a pattern not seen as clearly for the titanium electrodes.

Current efficiency for hydrogen evolution at low chromate concentrations

In the chlorate process the product chlorate salt is separated from the electrolyte by crystallization, and as the electrolyte contains Cr(VI), small amounts of chromate will co-precipitate or adsorb onto the chlorate crystals and end up in the chlorate product. A CrO_4^- concentration of as low as 9 mg dm^{-3} (80 µM Cr) in the electrolyte has been shown to be enough to form a chromium hydroxide film that hindered the reduction of nitrate and nitrite [14].

Potential sweep experiments were made on titanium in electrolytes with varying Cr(VI) concentrations (Figure 7) to study the effect of low Cr(VI) concentrations in chlorate electrolyte. In the 5 M NaCl electrolyte with 15 mM hypochlorite there was a limiting current for hypochlorite reduction. This electrolyte was Cr(VI) free and there was no inhibition of hypochlorite reduction. A similar sweep was made in chlorate electrolyte made from commercial grade $NaClO_3$ and p.a. grade NaCl, and showed that hypochlorite reduction was inhibited in the presence of 550 g dm^{-3} $NaClO_3$.

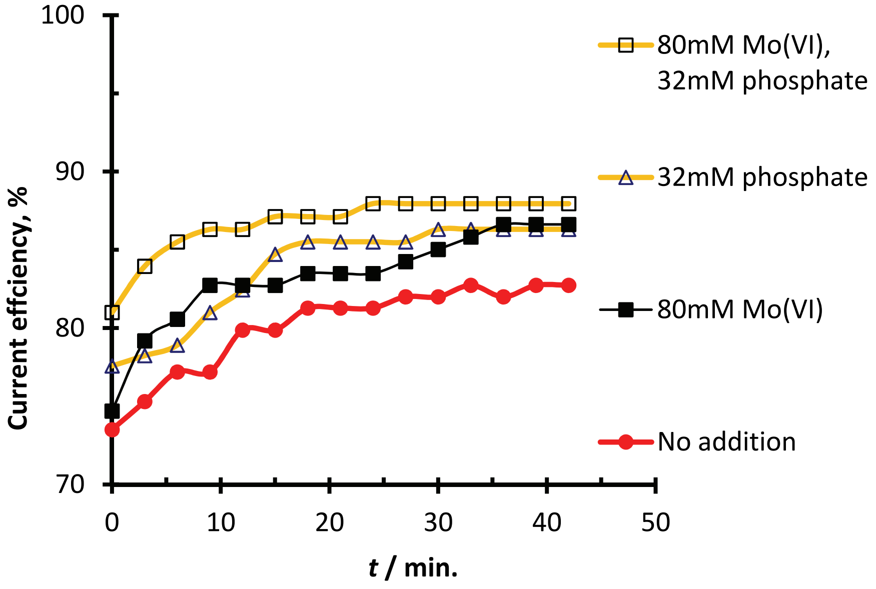

Figure 6. *Current efficiency measurements for hydrogen evolution on a stationary steel electrode at -3 kA m^{-2} in 1.6 M NaCl, 70 °C. Initially: [hypochlorite] ≈80 mM, pH 6.5*

From ICP analyses of the chlorate crystals it was calculated that this electrolyte contained also about 20 µM Cr(VI) and this inhibition was reproduced by adding 20 µM Cr(VI) to 5 M NaCl, see Figure 7. Thus, the inhibition of hypochlorite reduction on titanium in chlorate electrolyte without added Cr(VI) was caused by the Cr(VI) traces in non-recrystallized chlorate salt. Experiments were also made with an electrolyte made from $NaClO_3$ that had been recrystallized by cooling crystallization in the lab. For electrolytes with recrystallized chlorate the limiting current for hypochlorite reduction was higher, but the chromate effect was still there. This makes it difficult to evaluate Cr(VI) free alternatives using chlorate salt produced from a conventional industrial process with Cr(VI) containing electrolyte and the present study thus only considers hypochlorite reduction (reactions 6 and 7) and not chlorate reduction (reaction 8).

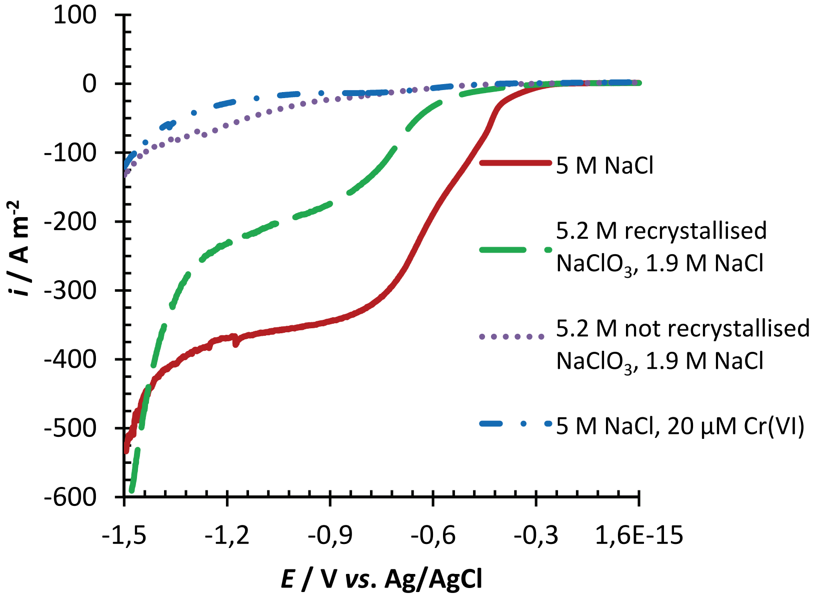

Figure 7. *Potential sweeps (anodic direction) using a Ti-RDE at 3000 rpm and 70 °C in electrolytes containing 15 mM hypochlorite performed with a sweep rate of 50 mV s^{-1}. Pre-polarization at -1.5 V* vs. *Ag/AgCl for 5 min.*

The effect of low levels of Cr(VI) was also studied in CE measurements on a steel electrode, see Figure 8 where a curve representing Mo(VI) additions has been added for comparison. The addition of 2.7 µM Cr(VI) increased the CE, as measured after 20 min of electrolysis, from about 80 % to over 94 %. This can be compared to 80 mM Mo(VI), which only increased the CE to about 83 % despite being present in a concentration about 30000 times higher. Increasing the Cr(VI) level to 27 µM increased the CE to 97 % after 20 min of electrolysis. With the lower Cr(VI) concentration it took over 10 min to reach steady state CE values, whereas for 27 µM Cr(VI) a high CE was reached instantaneously (in less than 1 min). Adding 80 mM Mo(VI) to the Cr(VI) containing electrolyte did not have a negative effect on the CE, but instead a small positive effect. Note that the high CE values obtained in these experiments relate to a steel cathode that had been polished prior to experiments and submerged into the electrolyte under cathodic polarization to avoid steel corrosion. In an earlier study it was found that the selectivity for hydrogen evolution on steel in chlorate electrolytes was highly dependent on whether the steel surface had been allowed to corrode prior to the measurements [11]. Hydrogen evolution was suppressed on corroded steel, in favor of electrochemical chlorate reduction. Compared to non-corroded steel, much higher concentrations of Cr(VI) was needed in the electrolyte to obtain high current efficiencies for hydrogen evolution. Thus, in the present study, if the electrode had been allowed to corrode on open circuit in hypochlorite containing electrolyte, the CE values would have been lower and probably the very low Cr(VI) levels in the present study would have had a negligible effect on the CE. Not only corroded steel but also RuO_2 prepared by thermal decomposition have shown a low selectivity for hydrogen evolution in chlorate electrolytes [15]. However, if a smooth and relative stable substrate material, free from oxides catalyzing chlorate reduction, is used the Cr(VI) level in the chlorate process may be lowered substantially while maintaining a high CE. This seems true also for Mo(VI) addition and therefore it will be difficult to replace Cr(VI) in the existing process without replacing the steel cathodes with a more dimensionally stable material. We have earlier shown that Mo(VI) addition can activate a substrate so it will have a similar activity for HER as iron [7], thus less active materials can be used instead of iron/low alloyed carbon steel.

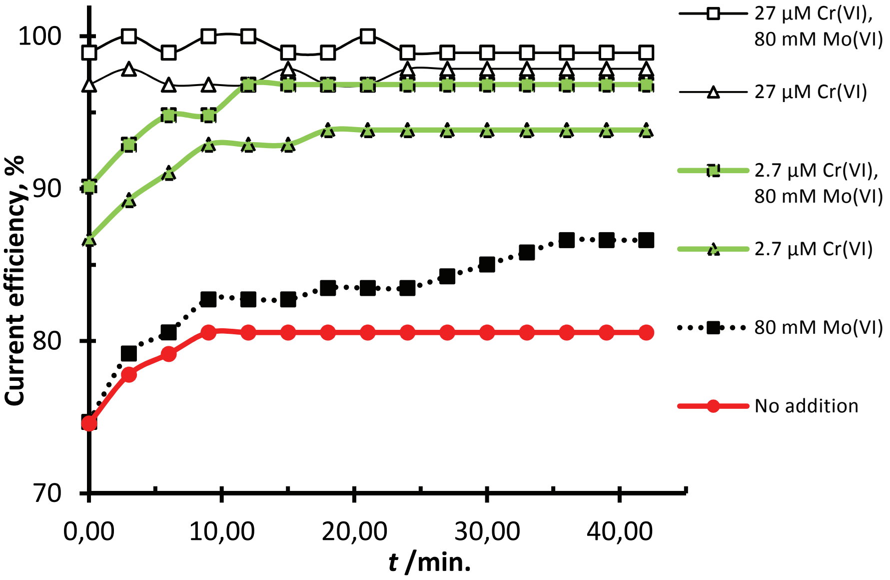

Figure 8. *Current efficiency measurements for hydrogen evolution on a stationary steel electrode at -3 kA m^{-2} in 1.6 M NaCl at 70 °C. Initially: [hypochlorite]≈80 mM, pH 6.5*

Surface analysis by SEM and EDS

In Figure 9 SEM micrographs of films obtained on a titanium cathode are shown. Figure 9 a, shows the bare titanium surface prior to any contact with the electrolyte and is given for comparison. The other micrographs show the cathode surface after 20 min of electrolysis at -3 kA m^{-2} in 5 M NaCl with different additives. With 80 mM Mo(VI) in the electrolyte a dense Mo-containing film, covering the cathode surface, was formed (Figure 9 b). The cracks seen are most probably due to drying of the film. With 32 mM phosphate in the electrolyte a totally different surface appears with needle-like crystals, see Figures 9 c and 9 d (larger magnification). In the presence of both Mo(VI) and phosphate in the electrolyte there is again a dense film (figures 9 e and 9 f), now with a spotted appearance.

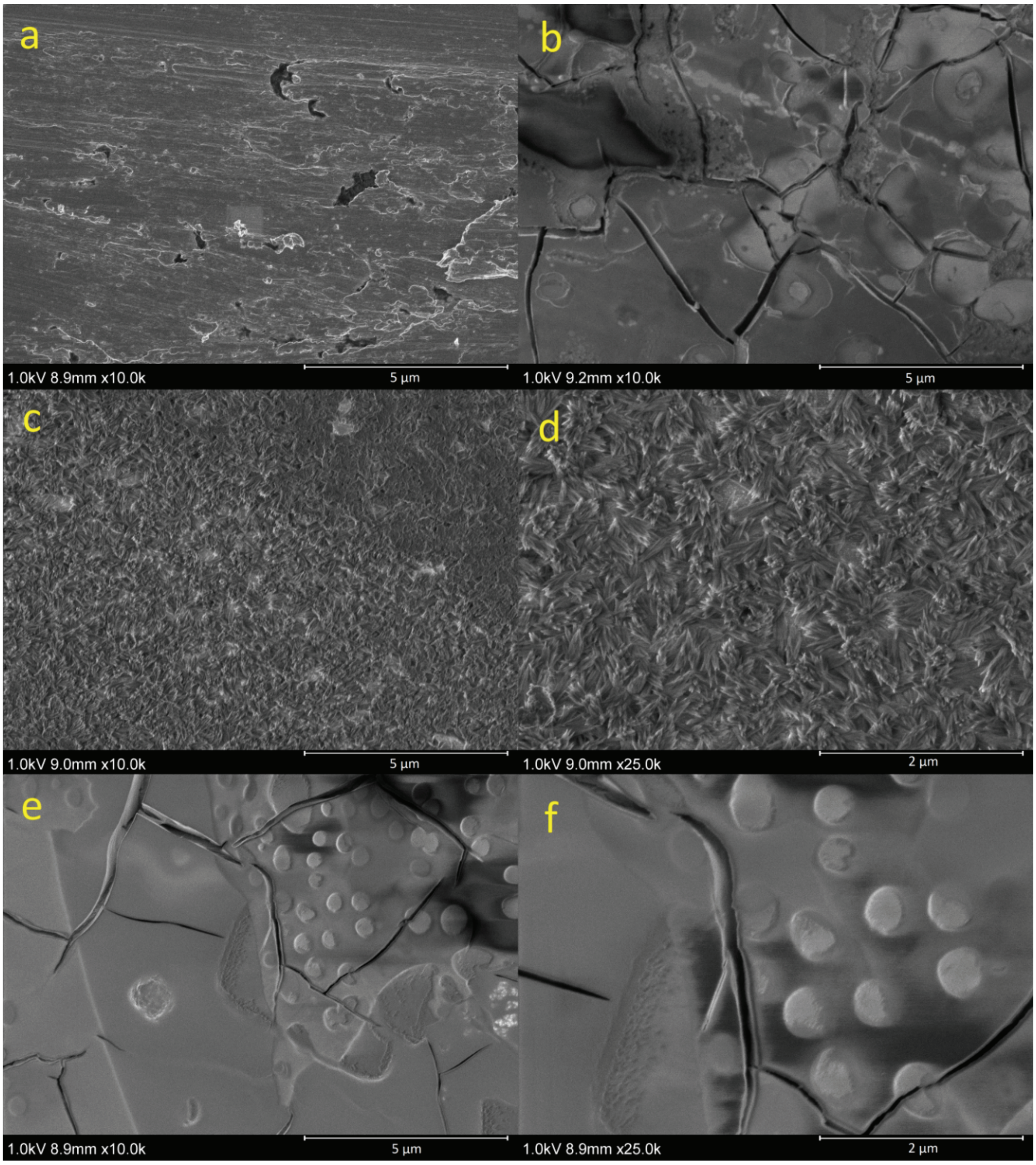

Figure 9: SEM images of titanium electrodes polarized at -3 kA m^{-2} for 20 min at 70 °C in 1.6 M NaCl with 100 mM hypochlorite and the following electrolyte additions: 80 mM molybdate (9 b); 32 mM phosphate (9 c-d); 80 mM molybdate + 32 mM phosphate (9 e-f). The sample in 9 a shows, for comparison, a polished titanium surface not exposed to electrolyte.

Elemental analyses with EDS showed that the films formed in the presence of Mo(VI) all contained Mo to a large extent (Table 1). The film formed in the presence of Mo(VI) and phosphate also contained P and was thinner than the film formed when only Mo(VI) was present. Looking at the sample with only phosphate addition, Figures 9 c,d and Table 1 the compounds phosphorous and oxygen were present in a molar ratio of 1:4 and thus phosphorous was likely present as phosphate in the cathode film. For comparison a sample was just dipped, with no cathodic polarization, into the electrolyte with 32 mM phosphate. No needle-like crystals were observed when examining the sample in the SEM and no phosphorous could be detected by EDS (not shown in Table 1).

Table 1. *Elemental analysis with EDS on titanium electrodes polarized at -3 kA m^{-2} for 20 min at 70 °C in 1.6 M NaCl with 100 mM hypochlorite and electrolyte additions according to table. The values are given in atomic %.*

Element	*80 mM Mo(VI)	*80 mM Mo(VI)+32 mM PO_4^{3-}	**32 mM PO_4^{3-}
O	56.6	61.7	64.9
Ti	14.0	18.4	-
Na	12.7	10.7	5.5
Cl	8.8	2.3	-
Mo	7.5	5.1	-
P	-	1.8	15.9

* Acceleration voltage: 15 kV **Acceleration voltage: 5 kV

In an earlier publication we found that if phosphate was added to a Mo(VI)-containing electrolyte, no molybdenum containing films could be detected with EDS on the cathode surface [7]. In that case the phosphate concentration was 2.5-10 times higher than the molybdate concentration. In the CE measurements in the present work, 20 times higher molybdate concentration (80 mM Mo(VI)) was used than in the previous study (4 mM Mo(VI), Ti-RDE 3000 rpm, and no added hypochlorite [7]) and therefore molybdate can be favored in a competitive adsorption between molybdate and phosphate.

In the presence of both molybdate and phosphate in the electrolyte there were also some larger circular spots on the electrode surface (Figure 10). The spots were around 10 µm in diameter and darker than the surrounding film (image taken in back-scatter mode). EDS analysis showed that the molybdenum level was higher in the spots that in other areas of the film. The spot can be an elevated structure, dramatically increasing film thickness.

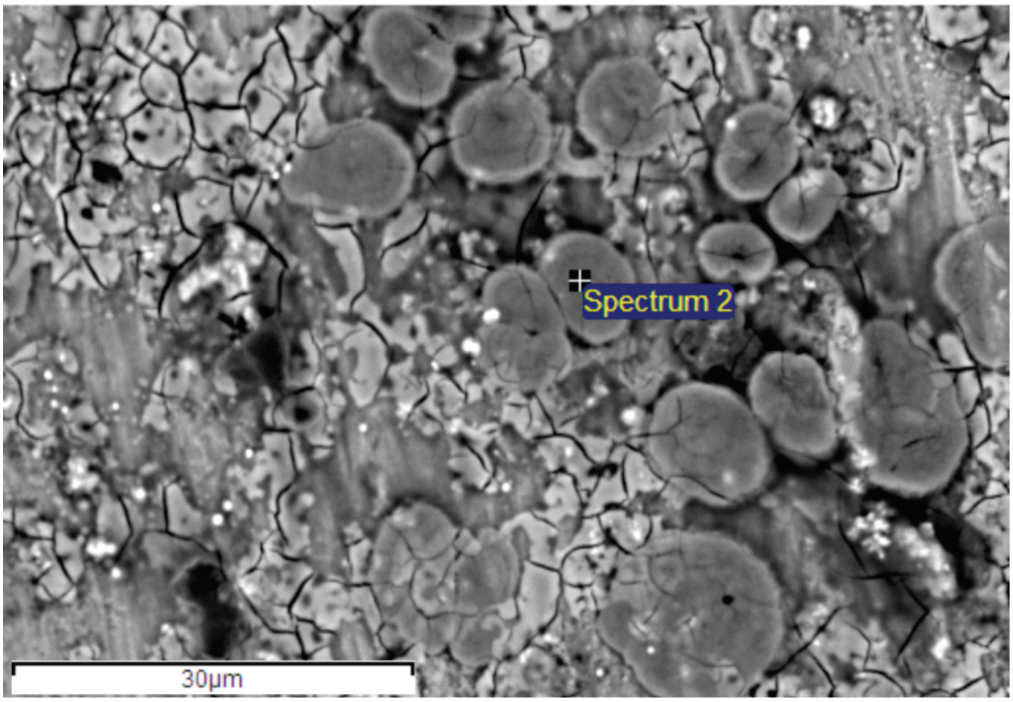

Figure 10. *SEM image in back-scatter mode of a titanium electrode polarized at -3 kA m^{-2} for 20 min at 70 °C in 1.6 M NaCl with 100 mM hypochlorite, 80 mM Mo(VI) and 32 mM phosphate.*

Effects of molybdate on the anode potential

Since chlorate cells are undivided, the anode will encounter the same electrolyte as the cathode. Thus any effects on the anode reactions that the electrolyte additives may have are important to study, and Mo(VI) at high concentrations have shown to increase the oxygen levels in the off gas [6],[8]. Oxygen may form from several different reactions on the anode or in homogeneous reactions in the electrolyte [1] and experiments were made to evaluate if the high oxygen values are accompanied by an increase in anode potential. The anions $Cr_2O_7^{2-}$, PO_4^{3-} and NO_3^- have been observed to increase the oxygen levels in the off gas in chlorate electrolysis, probably caused by anodic oxygen evolution and the likely mechanism suggested was an adsorption of the anions on the anode surface [16]. In another study an increased anode potential of about 15 mV was observed when increasing the Cr(VI) concentration from 3 to 9 g dm^{-3} $Na_2Cr_2O_7$ for a DSA in an electrolyte of pH 2 [10].

To study anode effects of Mo(VI), RuO_2/TiO_2 electrodes produced by spin coating and shaped into RDEs were polarized at 3 kA m^{-2} for 30 min with and without 40 mM Mo(VI) in the electrolyte. The addition of Mo(VI) resulted in an increase in anode potential around 40 mV, see Figure 11. Using SEM, no clear morphology change due to film formation or deposits could be seen on the RuO_2/TiO_2 surfaces, although Mo/Na ratios 2-10 times larger than expected from electrolyte composition were measured with EDS. Also XRF measurements indicated increased molybdenum content on the surface. Furthermore predominance diagrams show $MoO_3 \cdot 2H_2O(s)$ as the dominant phase in 10 mM Mo(VI) solution if the conditions are acidic and oxidizing [17], such as close to the anode. It is thus likely that the increased oxygen is caused by precipitation or adsorption of Mo-containing species on the anode surface.

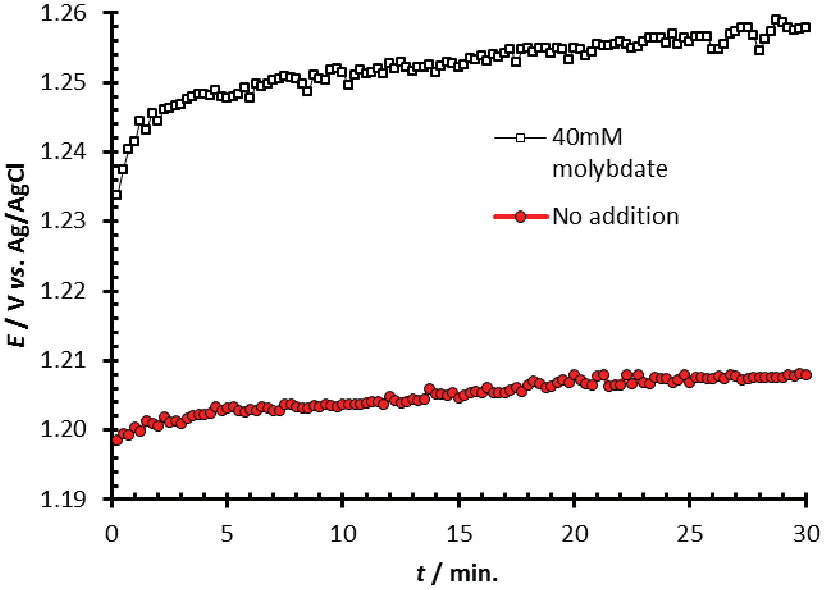

Figure 11. *Galvanostatic polarizations of DSA-RDEs (spincoated 3-layers) at 3 kA m^{-2} in 2 M NaCl, pH 7, 70°C at a rotation rate of 3000 rpm.*

Conclusions

The presence of Mo(VI) ions in an electrolyte of near neutral pH can increase the selectivity for hydrogen evolution as the Mo-containing film formed on the cathode surface hinders the side reaction of hypochlorite reduction.

Potential sweeps and current efficiency experiments in neutral electrolytes show that on a smooth substrate such as polished titanium the suppression of hypochlorite reduction by Mo(VI) addition is more efficient than on steel or on corroded iron.

Even very low levels of Cr(VI), in the μM range, can efficiently suppress hypochlorite reduction on polished titanium and steel. Thus if using smooth and stable cathode materials the chromate concentration on the chlorate process may be substantially reduced compared to the levels used today (1-6 g dm^{-3} $Na_2Cr_2O_7$ corresponding to about 10-50 mM Cr(VI)). Note though that the reaction of electrochemical chlorate reduction has not been addressed in the present study. The inhibiting action of very low Cr(VI) concentrations also means that when studying alternatives to Cr(VI) in the chlorate process possible Cr(VI) present in the chlorate salt used to make the electrolyte in the experiments should be considered. Mo(VI) on the other hand needed higher concentrations and longer polarization times to show an effect on the current efficiency.

Phosphate, a possible buffer needed in the chlorate process if removing, or substantially lowering the concentration of, Cr(VI) does not negatively influence the current efficiency in the presence of Cr(VI) or Mo(VI). Instead a slight increase in current efficiency was noticed when adding 32 mM NaH_2PO_4 to the electrolyte. The Mo-containing cathode films formed during cathodic polarization become thinner if the electrolyte during the film build-up also contained phosphate, but the films still appeared as effective at hindering hypochlorite reduction.

The presence of Mo(VI) in the electrolyte can increase the potential of a RuO_2-TiO_2 anode. The anode potential increased 40 mV after adding Mo(VI) corresponding to 40 mM, a concentration that in a previous study [6] resulted in increased oxygen levels in the off gas. Thus the increased oxygen production is likely produced in an anodic side reaction promoted by the adsorption of Mo(VI) species on the anode.

Considering increased oxygen levels and increased cathode and anode potentials, if Mo(VI) is to be used in the chlorate process it should be used at a low concentration to minimize the negative side effects.

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