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Rare earth metal salts as potential alternatives to Cr(VI) in the chlorate process

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Abstract Chromate is today added to industrial chlorate electrolyte, where it forms a thin cathode film of chromium hydroxide that hinders unwanted reduction of hypochlorite and chlorate. The aim of this study was to investigate rare earth metal (REM) ions as an environmentally friendly alternative to the toxic chromate addition. Potential sweeps and iR-corrected polarisation curves were recorded using rotating disc electrodes of iron and gold. Addition of Y(III), La(III) or Sm(III) to 5 M NaCl at 70 °C suppressed hypochlorite reduction. Activation of hydrogen evolution by REM ion addition to 0.5 M NaCl was more significant at 25 °C than at 50 and 70 °C. Increasing the chloride concentration to 5 M had a detrimental effect on this activation. The major problem in replacing chromate with REM salts is the poor solubility of REM ions at normal chlorate process conditions, and therefore REM salts are not a realistic alternative to chromate addition.

Keywords Rare earth metals · Chlorate production · Yttrium · Hydrogen evolution · Hypochlorite · In situ electrodeposition

1 Introduction

1.1 The chlorate process

In electrolytic sodium chlorate production, chloride ions are oxidized on the anode, and chlorine formed dissolves and reacts further to form hypochlorite and chlorate in the electrolyte bulk (reactions 1–4). The main cathode reaction is hydrogen evolution from water (reaction 5). Hypochlorite and chlorate reduction are unwanted side reactions on the cathode (reactions 6 and 7) [1].

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow ClOH + Cl^- + H^+ \quad (2)$$

$$ClOH \leftrightarrow ClO^- + H^+ \quad (3)$$

$$2ClOH + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \quad (4)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (5)$$

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

$$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^-. \quad (7)$$

The electrolyte consists of about 500–600 g/dm^3 $NaClO_3$, 100–120 g/dm^3 NaCl, 1–7 g/dm^3 NaClO and 3–10 g/dm^3 $Na_2Cr_2O_7$ at a pH of 6–7 and a temperature of 70–90 °C. The chromate serves several purposes [1], one of which is to reach a high current efficiency of the process. During polarisation Cr(VI) is reduced to Cr(III) and forms a film on the cathode, which hinders the electrochemical reduction of hypochlorite and chlorate ions [2]. The film is thin, in the order of 10 nm on platinum and gold, and has been shown to have the composition $Cr(OH)_3 \cdot xH_2O$ [3]. Hydrogen evolution can take place in the presence of the film, with changed kinetics compared to that on the bare cathode material. A higher overpotential for hydrogen evolution was obtained for iron and platinum in the presence of Cr(VI), whereas less effective electrocatalysts such as gold and lead were activated by the film [4]. As Cr(VI) is ecologically harmful, carcinogenic and reprotoxic, it should in the future preferably be replaced with a more environmentally friendly alternative.

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In the early days of chlorate production addition of calcium carbonate to the electrolyte was used to increase the current efficiency. Calcium hydroxide forms a diaphragm at the cathode surface, thus obstructing the reduction of hypochlorite [5]. Another suggested alternative to chromate is Mo(VI), which is claimed to have synergistic effects with Cr(VI) in increasing the current efficiency [6]. Recently sodium molybdate was investigated as a replacement for chromate but observed to lower, rather than raise, the current efficiency in the chlorate process [7]. The use of phosphate to replace chromate was found to increase both the selectivity and the activity for hydrogen evolution on cathodes made of an iron–molybdenum alloy [8]. According to the authors, phosphate formed a film on the cathode inhibiting hypochlorite reduction.

Since the introduction of DSA anodes the major voltage loss in the chlorate cell is related to the cathode overpotential for hydrogen evolution. Today low carbon steel or titanium are the dominating cathode materials, but with a ruthenium activated cathode the overpotential may be reduced by 200–300 mV [9]. Despite much effort there is no such cathode available on the market, mainly due to long term stability problems encountered. Nevertheless, there is a strong need to lower the cathode overpotential.

Ideally, the alternative to chromate would be a less toxic compound that inhibits the unwanted hypochlorite and chlorate reduction while activating hydrogen evolution. It should be easy to implement in existing chlorate technology.

1.2 Effects of electrolyte additions of rare earth metal (REM) ions

Rare earth metals (REM) have been suggested as environmentally friendly alternatives for hexavalent chromium in corrosion research and are today used in some limited corrosion applications. The general mechanism for corrosion protection described [10–12] is that dissolved REM ions precipitate as a REM hydroxide film on cathodically polarized surfaces. In reactions such as oxygen reduction (reaction 8) or hydrogen evolution (reaction 5) hydroxide ions are produced, resulting in an alkaline electrolyte close to the cathode surface that enables precipitation of REM hydroxides. The formed films suppress reduction of dissolved oxygen [10–15], a cathode reaction in electrochemical corrosion.

In aqueous solutions, the only stable oxidation state for the rare earth metals yttrium, samarium and lanthanum is +3. In Table 1 the relevant E^0 values for oxidation of the metals are presented. The E^0 value for reduction of Sm^{3+} to Sm^{2+} is −1.55 V versus NHE [16].

Table 1 Properties of REM ions in water solutions

	E°/V versus NHE (M/M^{3+}) [16]	Log K_{sp} [17][a]	Calculated pH of precipitation (10 mM M^{3+})
Y	−2.372	17.5	6.50
La	−2.379	20.3	7.43
Sm	−2.304	16.5	6.17

[a] For the reaction $M(OH)_3(s) + 3H^+ \leftrightarrow M^{3+} + 3H_2O$

Yttrium hydroxide films formed by cathodic precipitation are essentially transparent, gel-like and contain high amounts of water. SEM pictures display cracked surfaces, due to shrinkage while drying in air and in the SEM [15]. Thermo gravimetric analysis (TGA) of cathodically precipitated films showed five weight-loss steps as the hydroxide gradually transformed into yttrium oxide, Y_2O_3 [18]. These results combined with differential scanning calorimetry (DSC) analyses suggested that the deposited films consisted of $Y(OH)_3{\cdot}3H_2O$. X-ray diffraction (XRD) analyses of the gel-like $Y(OH)_3$ films showed that they were essentially amorphous [18].

In a previous study, we found that addition of yttrium chloride salt to 0.5 M NaCl solutions at 25 °C hinders not only oxygen reduction (reaction 8), but also the reduction of hypochlorite, nitrate and protons (reactions 6, 9, 10) on iron cathodes [19]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{8}$$

$$NO_3{}^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{9}$$

$$2H^+ + 2e^- \rightarrow H_2. \tag{10}$$

It has recently been shown that addition of REM(III) salts to the electrolyte activates the hydrogen evolution reaction (HER). Yttrium nitrate addition appears to activate the HER on steel [13–15] and gold [13] as well as on a nickel base alloy [18]. Tran et al. [13] and Hsu et al. [18] suggest that the activation of HER is caused by diffusion of yttrium water complexes, reacting at the surface (reactions 11 and 12):

$$Y(H_2O)_x^{3+} + 3e^- \rightarrow Y(H_2O)_{x-3}^{3+} + 3/2H_2 + 3OH^- \tag{11}$$

$$Y^{3+}(H_2O)_{3+x} + 3e^- \rightarrow Y(OH)_3{\cdot}xH_2O + 3/2H_2. \tag{12}$$

According to Tran et al. [15] there was a linear relationship between the logarithm of the REM-nitrate concentration and the “onset potential” for hydrogen evolution in 0.5 M NaCl, indicating that the reactions were under mass transport control. However, experiments with $Y(NO_3)_3$ addition may be hard to interpret due to the difficulty in separating nitrate reduction from hydrogen evolution [19]. Therefore we [19] confirmed the activation of the HER from water in nitrate-free 0.5 M chloride solutions. Thus, the Y(III) addition activates hydrogen evolution from water, reaction 5, while hindering hydrogen evolution from protons, reaction 10.

Electrolyte addition of REM salts may increase the energy efficiency of hydrogen evolving cathodes in two ways simultaneously, by increasing the current efficiency and by lowering the overpotential for hydrogen evolution. This is very attractive for industrial electrolysis, such as the chlorate process.

The activating effect on HER of Y(III) and inhibition of nitrate reduction, hypochlorite reduction and proton reduction has earlier been investigated at 25 °C and 0.5 M Cl [19]. In the present study we approach conditions more relevant for the chlorate process, i.e. measurements in an electrolyte at 70 °C and at a higher ionic strength, to evaluate the potential of practical use of these promising properties. At 70 °C chlorate reduction is an important side reaction on steel cathodes, and it is of interest to study whether also that reaction is suppressed by the REM films.

The focus in this paper is on Y(III) addition, but there is also included some measurements on La(III) and Sm(III) addition. Even if iron is a more relevant electrode material than gold, gold is used as a more inert material to verify the suppression of hypochlorite reduction.

2 Experimental

For all experiments with rotating disk electrodes (RDE), electrode rotator Model 616 from EG&G Parc with a rotation rate of 3,000 rpm was used. The iron (diameter 5 mm) and gold (diameter 4 mm) electrodes were embedded in Teflon®. The experimental cell was a jacketed glass cell connected to a water bath for temperature control. As the counter electrode a platinum grid was used and the reference electrode was an Ag/AgCl electrode (K201 from Radiometer) with saturated KCl at room temperature connected to a Luggin capillary.

The electrolytes were made from MilliQ water; pro analysis grade sodium chloride, pro analysis grade sodium perchlorate, both from Merck; sodium chlorate from Eka Chemicals AB; yttrium(III)chloride hexahydrate 99.99%, samarium(III)chloride hexahydrate 99.99+ %, lanthanum(III)chloride heptahydrate 99.999%; all from Sigma-Aldrich and NaClO stock solution from BDH Laboratory Supplies. The sodium chlorate was re-crystallized for purification. The NaClO stock solution, analyzed with arsenite titration, was found to contain 35 g/dm^3 NaClO. In experiments made using chloride containing electrolyte hypochlorite was also generated during the experiment. In this paper the word "hypochlorite" refers to the sum of the species ClO^- and HClO. Adjustments of pH in the electrolytes were made with additions of NaOH and HCl. For all solutions the concentrations are valid at room temperature, with the exception of potential sweeps in 550 g/dm^3 $NaClO_3$, 110 g/dm^3 NaCl solutions which had valid concentrations at 70 °C.

Potential sweep experiments were made with a PAR 263A potentiostat controlled by the Corrware software package. In all experiments the electrolyte was purged with N_2 for 15 min prior to the sweeps. The gold RDE was polished with alumina paste (Alpha micropolish No. 1C, particle size 1.0 micron from Buehler), washed in an ultrasonic bath with acetone and thoroughly washed with MilliQ water. Before starting the sweeps, the electrode was prepolarised for 1 min at −1.5 V versus Ag/AgCl. The iron RDE was polished with 4000 grade TiC paper, thoroughly washed with water and prepolarised for 2 min at −1.5 V versus Ag/AgCl before starting the sweeps.

In all polarisation curve experiments the electrolyte was purged with N_2 for 15 min prior to and during the measurements. The iron RDE was polished using 4000 grade TiC paper and thoroughly washed with milliQ water. The iron RDE was cathodically prepolarised for 1 min at the initial current density of 5 kA/m^2, before recording a curve of 41 fixed current steps of 15 s at each point between 5 kA/m^2 and 0.5 A/m^2. Polarisation curves were recorded with a PAR 273A potentiostat controlled by a PC, and ohmic drop correction was done with a current interrupt technique [20]. All polarisation curves were recorded in the anodic direction, from the highest to the lowest current density.

Current efficiency measurements were made by measuring the gas produced in the cathode compartment of a divided glass cell. The half-cells were divided by a Gore L-596 Seratex porous electrochemical diaphragm. A calibration curve was made in 1.2 M $NaSO_4$ by measuring the time needed to collect 5 mL hydrogen gas at different current densities with a platinum wire cathode and assuming 100% current efficiency for the HER. This curve was used to evaluate the current efficiency from experiments in 550 g/dm^3 sodium chlorate solution. In these experiments the cathode was a stationary electrode, made of a low carbon steel grade >99% iron and partially covered by epoxy with a free surface area of 6.6 cm^2, or a titanium rod coated with RuO_2 (3 cm^2) [9]. A platinum wire was used as counter electrode.

The stability of 3.5 g/dm^3 sodium hypochlorite in the presence of 15 mM yttrium chloride in 0.5 M NaCl was tested at room temperature, to exclude catalysis of homogeneous hypochlorite decomposition in the presence of Y(III). Two solutions of 0.5 M NaCl, 3.5 g/dm^3 NaClO at pH 5 were prepared, to one of which 15 mM YCl_3 was added. After 20 h the solutions were analyzed with respect to sodium hypochlorite concentration. In the yttrium-free solution, the sodium hypochlorite concentration was

2.9 ± 0.1 g/dm^3, and in the yttrium-containing solution 3.0 ± 0.1 g/dm^3. Thus there was no significant increase in the rate of homogenous hypochlorite decomposition in the presence of Y(III).

In the polarisation curves and in the text cathodic currents have been written with positive sign, while for the potential sweeps in Figs. 1 and 2, negative sign was used.

3 Results and discussion

3.1 Inhibition of parasitic reactions

Suppression of hypochlorite reduction was investigated on a noble metal electrode, a gold electrode, as well as on the industrially more relevant iron. The electrodes were first prepolarised to build up a hydroxide film and then fast cyclic voltammograms were recorded to measure the limiting current for hypochlorite reduction. As shown in Fig. 1, the potential sweep for a gold RDE in 5 M NaCl at 70 °C started with hydrogen evolution at low potentials, reached a current plateau close to zero current at intermediate potentials and chlorine/oxygen evolution at high potentials. When adding hypochlorite to an electrolyte concentration of 1 mM NaClO a limiting current of about 3 mA/cm^2 appeared. This current for hypochlorite reduction was suppressed by the addition of 1 mM of either YCl_3, $SmCl_3$ and $LaCl_3$ and thus even small additions of rare earth metal salts can suppress hypochlorite reduction on a gold electrode. We have earlier found that under certain conditions around 10 mM of Y(III) is required for an activation of the hydrogen evolution reaction [19].

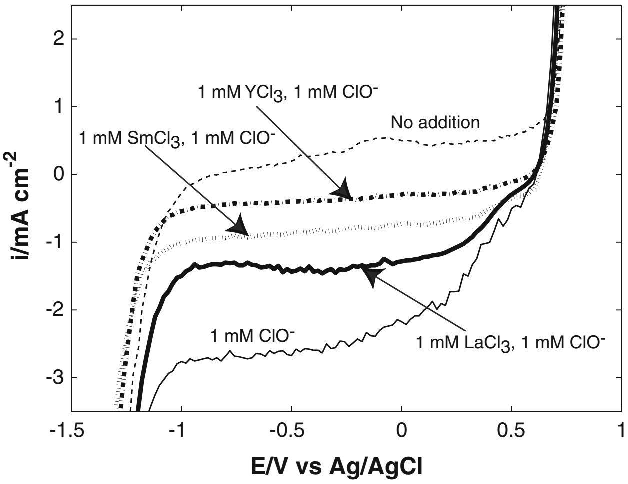

Fig. 1 Potential sweeps on a Au RDE at 3,000 rpm in 5 M NaCl at 70 °C, pH ≈ 5.8. Swept between −1.5 and 0.8 V at 50 mV/s. The sweeps in the cathodic direction are not shown, but the difference from the anodic sweeps was small

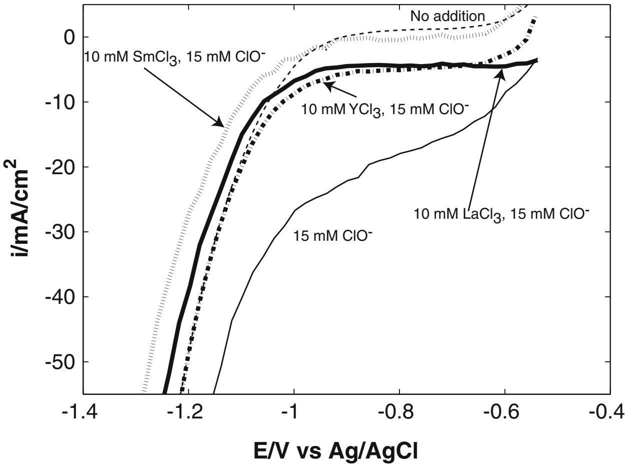

Fig. 2 Potential sweeps on a Fe RDE at 3,000 rpm in 5 M NaCl at 70 °C, pH ≈ 5.4. Swept between −1.5 and −0.5 V at 50 mV/s. The sweeps in the cathodic direction are not shown, but the difference from the anodic sweeps was small

Also under industrially more relevant conditions, iron cathode and higher hypochlorite concentration, REM salts can be used to suppress hypochlorite reduction (Fig. 2). Without cathodic protection iron will corrode in sodium chloride solutions; therefore a lower anodic limit potential was used for iron electrodes than for gold. Care should be taken when comparing the inhibiting effects in Fig. 2, since some bulk precipitation problems were noticed. The backward sweeps in cathodic direction (not shown in Figs. 1 and 2) had similar limiting currents for hypochlorite reduction as the sweeps in anodic direction, thus the hindering function remained after sweeps into the anodic region.

While hypochlorite reduction (reaction 6) can be studied using potential sweeps as in Figs. 1–2, chlorate reduction (reaction **7**) requires other techniques. Chlorate reduction takes place at more cathodic potentials, in a potential region coinciding with that of hydrogen evolution.

Assuming that hydrogen evolution and chlorate reduction are the only two cathode reactions occurring in an electrolyte of 550 g/dm^3 $NaClO_3$, the rate of chlorate reduction may be indirectly determined by measuring the volume of produced hydrogen gas. Results from such measurements are given in Fig. 3, showing that the current efficiency for hydrogen evolution steadily increased with time to reach approximately 65% after 2 h of polarisation (current efficiencies below 20% could not be measured with this experimental setup). The result is in agreement with earlier studies [4, 21, 22]. Reduction of chlorate is catalysed by iron oxides [21] and the catalytically active iron oxides that were initially present on the steel surface were probably reduced during polarisation.

Attempts were made to perform current efficiency measurements in a similar solution after addition of 10 mM

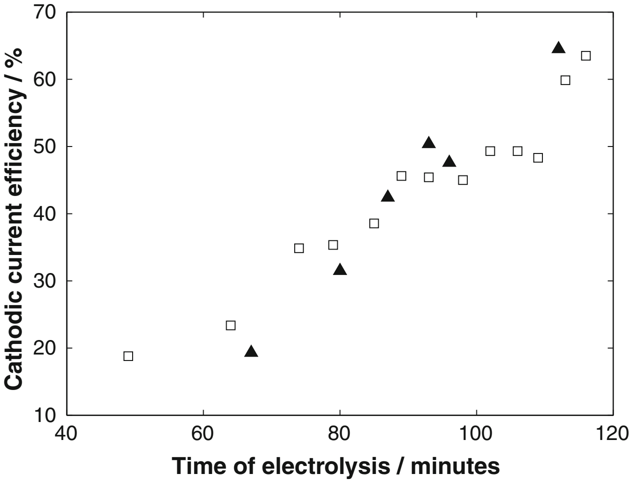

Fig. 3 Cathodic current efficiency for hydrogen gas evolution for a stationary steel electrode in 550 g/dm^3 $NaClO_3$ solution at t = 70 °C. Constant current density of i = 915 A/m^2 and two replicate experiments

YCl_3, to see if the yttrium hydroxide film could suppress also chlorate reduction. No clear effect was seen on the hydrogen production—the current efficiency was below 20%, with a few gas bubbles visible. A fine cloud of precipitates was noticed in the electrolyte at a distance from the cathode surface, and this was likely yttrium hydroxide precipitating in the bulk rather than on the cathode surface. When decreasing the current density ten times to 91.5 A/m^2 the same result was obtained. Ruthenium dioxide is known to be a catalytically active material for chlorate reduction with a very low current efficiency for hydrogen evolution in concentrated chlorate solutions at 70 °C [9], and any visible hydrogen gas formation in the presence of REM-salts would indicate a suppressed chlorate reduction. Therefore, a stationary ruthenium dioxide coated titanium rod [9] was used as cathode in 550 g/dm^3 sodium chlorate at 2 kA/m^2, 70 °C. No hydrogen bubbles could be seen either before or after addition of Y(III). However, again $Y(OH)_3$ precipitated as small particles in the electrolyte around the electrode rather than on the electrode surface.

The hydroxide diffusion layer is thicker around a stationary electrode than at an RDE, and therefore a pH high enough for precipitation of fine yttrium hydroxide particles was reached in the electrolyte at a distance from the stationary electrode. Thus the mass transport is important to obtain a thin enough diffusion layer for precipitation on the cathode surface.

In the case of Cr(VI) addition a chromium hydroxide film can easily be formed on a stationary electrode and there hinder chlorate reduction [4]. As opposed to yttrium hydroxide formation, the former is preceded by an electron transfer at the cathode where Cr(VI) is reduced to Cr(III), which precipitates as chromium hydroxide at the cathode surface. Formation of yttrium hydroxide is a simple chemical precipitation with no electrochemical step, and thus harder to direct to the cathode surface.

Previous results have indicated that a thin film is sufficient for hindering reactions as hypochlorite reduction [19]. Even though precipitation occurred in the electrolyte bulk, there may have been a thin film on the stationary cathode, enough to hinder certain reactions. Sodium chlorate was present at a high concentration, 550 g/dm^3, and therefore likely requiring a stronger barrier to hinder its reduction compared to hypochlorite, present at 15 mM NaClO. Thus our results indicate that either there was no yttrium hydroxide on the cathode surface, or the formed film was not sufficient to hinder chlorate reduction under the present conditions.

Polarisation curves in the potential region of hydrogen evolution and chlorate reduction were recorded to see effects of sodium chlorate and yttrium chloride additions, see Fig. 4. In 5 M NaCl the dominating reaction at high current densities is hydrogen evolution. The limiting current observed at ~10 A/m^2 is related to the reduction of hypochlorite, which was formed anodically during the measurements. When adding 100 mM $NaClO_3$ to the chloride solution the polarisation curve was displaced to higher potentials due to influence of chlorate reduction. Changing the electrolyte to 550 g/dm^3 $NaClO_3$ increased the potentials even more and, as expected, in the absence of chloride ions no limiting current for hypochlorite reduction appeared. Based on the results in Fig. 3 the dominating cathode reaction in 550 g/dm^3 $NaClO_3$ was probably chlorate reduction in these experiments, as they lasted for a relatively short time period.

The presence of 10 mM yttrium chloride in a 550 g/dm^3 sodium chlorate solution had a clear effect on the electrode

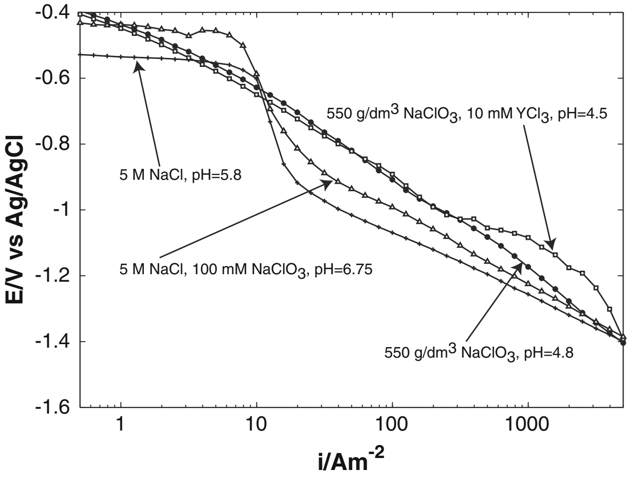

Fig. 4 IR-corrected polarisation curves on a Fe RDE at 70 °C. Electrode rotation rate 3,000 rpm

potential at high current densities, $> \sim 300$ A/m^2, see Fig. 5. When increasing the Y(III) concentration to 100 mM YCl_3, the potential became unstable and oscillation was observed at high current densities (curve not shown). This will be discussed more in the next section on activation of the hydrogen evolution reaction. The insignificant difference at lower current densities between chlorate solution with and without Y(III) can be explained in two different ways. On one hand the yttrium hydroxide film did not form, or if formed did not hinder the chlorate reduction. The second possibility is that the film activated hydrogen evolution and partly suppressed chlorate reduction at the electrode surface. To distinguish between these two theories product analyses are needed in experiments with a high mass transport rate at the electrode surface, so that yttrium hydroxide deposits on the cathode surface.

3.2 Activation of the hydrogen evolution reaction

The catalytic effect on hydrogen evolution by Y(III) addition was earlier studied at 25 °C in 0.5 M NaCl [19]. To approach more industrially relevant conditions first the effect of increased temperature was studied in 0.5 M NaCl, and later the chloride concentration was raised to 5 M NaCl. Polarisation curves in 0.5 M NaCl without and with 10 mM YCl_3 at varying temperature were recorded, and the curves made in the presence of YCl_3 are given in Fig. 5. At current densities > 100 A/m^2 there was no major effect of adding YCl_3 to the electrolyte, whereas at lower current densities the addition made the potential shift in anodic direction. As Y(III) is not redox active at these conditions, this shift is related to an activation of the hydrogen evolution reaction by Y(III) ions [19]. This catalytic effect clearly decreased with increasing temperature, and the same was found in similar experiments with electrolyte additions of 10 mM $SmCl_3$ and 10 mM $LaCl_3$ (curves not shown). For all three REM salt additions the activation was limited to current densities < 100 A/m^2, and it was also clear from the polarisation curves that hypochlorite reduction was hindered. The REM hydroxide film could easily be seen by the naked eye on the electrode surface after experiments at 25 °C, but not after trials at 70 °C. Likely it was dissolved at the higher temperature as the current was switched off.

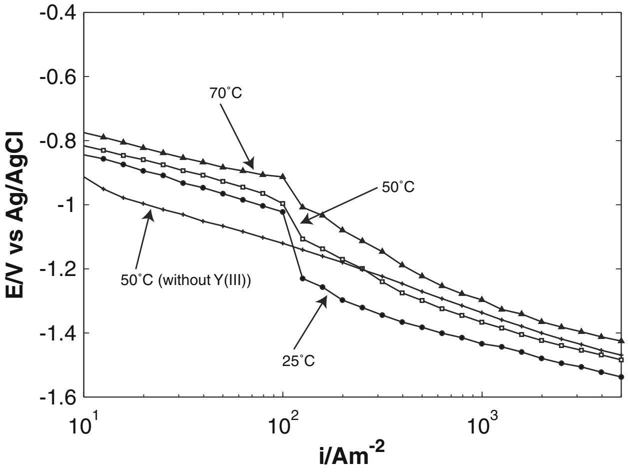

Fig. 5 IR-corrected polarisation curves on a Fe RDE in 0.5 M NaCl with 10 mM YCl_3 at varying temperatures. Electrode rotation rate 3,000 rpm

We have earlier shown that the activation of hydrogen evolution is independent of Y(III) concentration in the range 10–100 mM YCl_3, suggesting a catalytically active film with a reactant from within the film [19]. The lack of activation at current densities > 100 A/m^2 may be caused by the vigorous hydrogen gas evolution destroying the film. This is also supported by the results in Fig. 4, where an activation was observed even at high current densities when chlorate reduction, rather than hydrogen evolution, was the dominating reaction. The oscillation observed for 100 mM yttrium chloride in 5 M sodium chloride was probably due to a continuous formation and rupture of an yttrium hydroxide film. When formed, the film activated hydrogen evolution and suppressed chlorate reduction. Formed hydrogen bubbles in turn destroyed the film and chlorate reduction again became the dominating reaction. In the absence of vigorous gas evolution the film reformed etc. and this process led to the oscillating behaviour.

Increasing the chloride concentration from 0.5 to 5 M NaCl had an effect on the Y(III) activation at 25 °C. It became less distinct and the potentials were unstable when recording galvanostatic polarisation curves, which were difficult to reproduce. When raising the temperature to 70 °C the activating effect of Y(III) addition vanished—see the curve for 5 M NaCl at 70 °C in Fig. 6, showing an instant effect at ~ 100 A/m^2 that disappeared at lower current densities. To judge whether this behaviour was related to the high chloride concentration or to a high ionic strength in general, measurements were made in 5 M $NaClO_4$ at the same conditions.

In Fig. 6 the effect of high ionic strength and high chloride concentration are separated at 70 °C. The activation caused by Y(III) at <100 A/m^2, that disappeared when raising the chloride concentration to 5 M NaCl, was stable in 5 M $NaClO_4$. Thus it seems as the chloride ions at high concentration are detrimental to the catalysis. Note that the limiting current for hypochlorite reduction present in Fig. 6 disappeared in the presence of Y(III), indicating the presence of an inhibiting cathode film not disturbed by a high chloride concentration.

The negative effect above on the hydrogen evolution catalysis may be explained by adsorption of chloride ions blocking active sites on the electrode surface, or by the

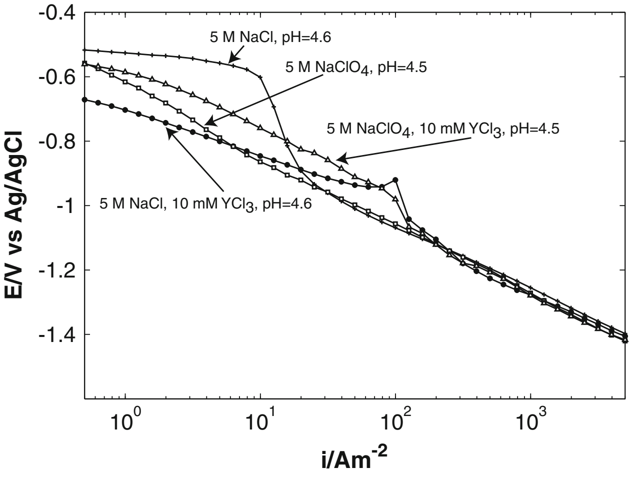

Fig. 6 IR-corrected polarisation curves obtained with a Fe RDE at 70 °C. Electrode rotation rate 3,000 rpm

formation of yttrium-chloride complexes that lower the concentration of active Y(III) species. If the reactant of the catalysed hydrogen evolution is water complex bound to REM cations, the activation may arise from the Lewis-acidity of the cation weakening the O–H bond [23]. The energy needed to reduce such complex bound water molecules is less than that needed to reduce free water.

The predominant Y(III)-forms in 5 M Cl^- at 25 °C are yttrium chloride complexes (reaction 13 etc), which could affect the build-up and composition of the film. Furthermore the Lewis acidity of YCl^{2+} and other yttrium chloride complexes may be weaker than Y^{3+}, thus water molecules in the hydration shell can be less polarised by the electron drawing cation [24].

$$Y^{3+} + Cl^- \leftrightarrow YCl^{2+} \quad \text{Log K} = -0.1. \tag{13}$$

In pure NaCl electrolyte the overpotential was slightly higher than in pure $NaClO_4$ electrolyte, see Fig. 6, probably due to adsorption of chloride ions on the electrode surface. Vračar and Dražić [25] have found that chloride ions adsorb on iron electrodes in sulphate electrolytes and increase the overpotential for hydrogen evolution.

3.3 Limitations in pH range

A solution of 550 g/dm^3 sodium chlorate with 100 mM YCl_3 had a pH of 3.7 at 70 °C as prepared. The pH was raised by dropwise addition of 0.5 M NaOH. At pH 4.8 a white precipitation of yttrium hydroxide was noticed, and with each droplet of hydroxide solution added an increased buffering effect was observed as pH increased more slowly. This result discouraged experiments at pH 6.5 and 70 °C, which is most relevant for the chlorate process. Potential sweeps on a iron RDE at 3,000 rpm made in a solution similar to industrial chlorate electrolyte (550, 110 g/dm^3 NaCl, pH 6.5 at 70 °C) but without Cr(VI) after addition of 15 mM NaClO and 10 mM YCl_3, showed no hindering effect on hypochlorite reduction by the Y(III) addition. Thus the Y(III) concentration after the precipitation in the bulk was too low for an $Y(OH)_3$ film to be formed on the cathode.

4 Conclusions

In situ formed cathode films of yttrium-, samarium- and lanthanum hydroxide can suppress hypochlorite reduction on iron and gold in electrolytes of high ionic strength (5 M NaCl and 5 M $NaClO_4$) and elevated temperature (70 °C). Current efficiency measurements, with product analysis, at adequate mass transport conditions are needed to quantify the inhibiting ability.

The hydrogen evolution reaction is activated by the REM salt addition, but to a smaller extent at 70 °C than at 25 °C. A high chloride concentration (5 M NaCl) is detrimental to the activating effect, in particular at elevated temperature.

The solubility of the REM ions is a challenge for industrial applications in several respects. First, the pH of the electrolyte bulk must be low enough for the REM species to be dissolved, but high at the cathode surface for the hydroxide film to precipitate. Second, in the absence of a strong convective mass transport the flat pH gradient will cause the metal hydroxide to precipitate in the electrolyte rather than in the electrode surface. Also, the REM-salts may precipitate with anions such as phosphate in the bulk. The fact that yttrium ions were not dissolved in 550 g/dm^3 $NaClO_3$, 110 g/dm^3 NaCl at pH 6.5 is a practical limitation to its use in chlorate electrolysis.

The current density range where activation of hydrogen evolution occurs is limited. A film seems to form at higher current densities if another reaction, not forming gas bubbles, dominates over water reduction. Probably the films are not stable during vigorous hydrogen evolution, thus a self-destructing mechanism of the catalytic film.

Addition of REM ions is not a realistic alternative to Cr(VI) in the chlorate process, mainly due to solubility problems.

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References

1. Coleman JE (1981) Tutorial lectures in electrochemical engineering and technology, vol 77, A.I.Ch.E. Symp. Ser. 204. Institute of Chemical Engineers, New York, p 244

2. Lindbergh G, Simonsson D (1991) Electrochim Acta 36:1985
3. Ahlberg Tidblad A, Lindbergh G (1991) Electrochim Acta 36:1605
4. Cornell A, Lindbergh G, Simonsson D (1991) Electrochim Acta 37:1873
5. Vogt H (1981) J Electrochem Soc 128:29C
6. Grotheer MP et al (1970) Sodium dichromate and molybdic acid to increase the cathode efficiency of chlorate cells, US Patent No 3,535,216
7. Li M, Twardowski Z, Mok F, Tam N (2007) J Appl Electrochem 37:499
8. Krstajic N, Jovic V, Martelli GN (2007) System for the electrolytic production of sodium chlorate, World Intellectual Property Organization Patent No WO 2007/063081 A2
9. Cornell A, Simonsson D (1993) J Electrochem Soc 140:3123
10. Hinton BRW, Wilson L (1989) Corros Sci 29:967
11. Zhang T, Li DY (2003) Mater Sci Eng A 345:179
12. Böhm S, Greef R, McMurray HN, Powell SM, Worsley DA (2000) J Electrochem Soc 147:3286
13. Tran M, Fiaud C, Sutter EMM (2006) J Electrochem Soc 153:B83
14. Tran M, Mohammedi D, Fiaud C, Sutter EMM (2006) Corros Sci 48:4257
15. Tran M, Dubot P, Sutter EMM (2008) Int J Hydrog Energy 33:937
16. Lide DR (2008) CRC handbook of chemistry and physics, 88th edn. CRC Press/Taylor and Francis, Boca Raton (Internet version)
17. Baes CF, Mesmer RE (1976) The hydrolysis of cations. Wiley, New York, pp. 124, 137
18. Hsu CT, Yen SK (2005) J Electrochem Soc 152:C813
19. Nylén L, Gustavsson J, Cornell A (2008) J Electrochem Soc 155:E136
20. Cornell A, Håkansson B, Lindbergh G (2003) Electrochim Acta 48:473
21. Tilak BV, Tari K, Hoover CL (1988) J Electrochem Soc 135:1376
22. Wulff J, Cornell A (2007) J Appl Electrochem 37:181
23. Wulfsberg G (2000) Inorganic chemistry. University Science Books, Sausalito, p 56
24. Smith RM, Martell AE (1976) Critical stability constants, Vol. 4: inorganic complexes, Plenum Press, New York, p 104
25. Vračar LJ, Dražić DM (1992) J Electroanal Chem 339:269