



Studies Relating to Cathodic Reduction of Hypochlorite in Neutral Chloride Solutions – Used in Chlorate Processes

Vasudevan S.

CSIR - Central Electrochemical Research Institute, Karaikudi - 630 006, INDIA

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Abstract

The inhibition effect of the chromium hydroxide film for the reduction of hypochlorite has so far been studied on gold, platinum and iron electrodes in sodium hydroxide and sodium chlorate solution. But there is no reports were available in the case of alkaline earth metal chlorates. In order to more clearly distinguish, the effects of the film, the addition of chromate and its effect on the cathodic reduction of hypochlorite in sodium and alkaline earth metal chlorates solutions, the studies were carried out in platinum electrode. It was found that the addition of chromate to the sodium chlorate solution suppresses the hypochlorite reduction by forming a thin layer of chromium hydroxide on the electrode surface. In the case of magnesium, strontium and barium chlorate solutions the hypochlorite reduction was suppressed even without the addition of chromate in the electrolyte due to the formation of corresponding metal hydroxides on the electrode surface.

Key words: cathodic reduction, chromate, chlorate, cyclic voltammetry, hypochlorite.

Introduction

Cathodic hydrogen and anodic chlorine evolution reactions, from neutral chloride media are primary reactions in the technology of chlorate production. Chromate and its electrochemical reduction are of practical importance in the industrial process for the production of alkali metal chlorates where chromate is added to the electrolyte, since this is empirically known to prevent the hypochlorite being reduced to chloride ions at the cathode surface. It was found that a thin film of $\text{Cr}(\text{OH})_3$ is formed, which hinders almost completely the hypochlorite reduction reaction at the cathode surface. A widely accepted explanation of this effect is that $\text{Cr}(\text{OH})_3$ acts as diaphragm on the cathode¹⁻⁷.

It is suggested¹ that the reduction of hypochlorite ions is prevented by an adverse potential gradient, which hinders the transport of the negatively charged ions into the cathode covered by a 'diaphragm'. It was found that the reduction of chlorate to be almost completely suppressed on a polymer coated steel cathode and the cathodic losses in the absence of chromate have been found to decrease with an increased current density^{8,9}. All these results can be explained by the effect of an increased potential gradient and seem to support the 'diaphragm' theory. It is reported that^{6,7} the effect of chromate addition on the hypochlorite reduction at a platinum electrode in alkaline solution obtain similar results. They found that reduced chromate formed a $\text{Cr}(\text{III})$ on the electrode surface, which suppressed not only the reduction of hypochlorite but also the reduction of several other negatively charged ions and uncharged molecules. This effect has also been observed with much lower concentrations of chromate than generally used in the chlorate process.

However, the effect of addition of chromate for hypochlorite reduction has not been studied extensively in alkaline earth metal chlorates. Hence, the cyclic voltammetric studies have been undertaken with sodium, magnesium, strontium and barium chlorides.

Material and Methods

A Princeton Applied Research (PAR) model 371 Potentiostat-Galvanostat and a Wenking Scan Generator (VSG 83) in combination with a Kontron digital multimeter for potential indicating and HIL 2103 multimeter for current indication were used. The curves were recorded using a X-Y/t recorder (Rikadenki, Japan).

All experiments were carried out in an ordinary three-electrode glass cell, under nitrogen atmosphere, which had an external jacket for circulation of water to maintain electrolyte temperature. Platinum wire embedded in Teflon (area = 0.126 cm^2) and platinum foil was used as working electrode and counter electrode respectively. Standard Calomel Electrode (SCE) was used as reference electrode. The working electrode was polished with alumina polish on micro cloth for 2 minutes and cleaned with distilled water. This was then followed by the ultrasonic cleaning for 5 minutes to remove any residual alumina particles from the surface and finally rinsed with acetone.

The experiments were carried out in 2M sodium, magnesium, strontium and barium chlorate (CDH) solutions, of 0.1L, at the scan rate of 50 mv.s^{-1} . Na_2CrO_4 supplied by Merck was used. The hypochlorite was added to the electrolyte and its concentration was determined by potentiometric titration. Cyclic Voltammograms were recorded at a temperature of $25 \pm 1^\circ\text{C}$ between the potential range of +0.9V to -1.0V (vs SCE).

Results and Discussion

During the electrolytic oxidation of chloride solution to obtain chlorate, the primary products of the anode and cathode reactions are chlorine and alkali respectively, which react in the bulk electrolyte between the electrodes to form hypochlorous acid and hypochlorite. These are subsequently reacting chemically to form chlorate⁴. The main reactions in the chlorate electrolysis process can thus be written as:

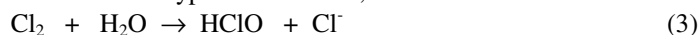
At the anode, (chlorine is formed)



At the cathode, (hydroxyl ions and hydrogen are formed)



At the bulk, chlorine ions formed at the anode react rapidly with water to form hypochlorous acid,

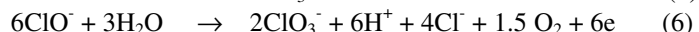
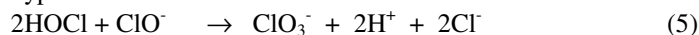


Since the electrodes are close together and have no diaphragm, the chlorine can react with hydroxyl ions formed at the cathode to produce hypochlorite ions,



As a result, the solution around the anode becomes strongly acidic and the solution in contact with the cathode is alkaline. In addition to this pH gradient, the concentration of hypochlorous acid also establishes a gradient relatively high around the anode and relatively low around the cathode.

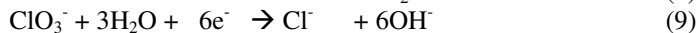
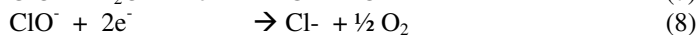
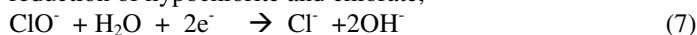
It is usually assumed that chlorate is formed by the reaction of hypochlorite ion by free hypochlorous acid (reaction 5) when pH is 6.0 to 6.5. However when pH is slightly alkaline the electrochemical formation of chlorate through discharge of the hypochlorite



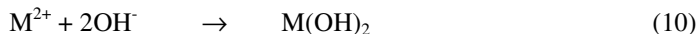
ion at a potential equal to that for discharge of the chloride ion (reaction 6).

According to reactions (5) and (6) chlorate may be formed in two ways, either by a purely chemical reaction of the hypochlorite ion with hypochlorous acid in the bulk solution (chemical chlorate formation) or by electrochemical oxidation of the hypochlorite at the anode under simultaneous oxygen evolution (anodic chlorate formation). If all chlorate is formed by the chemical reaction (5), 6 and 12 Faradays are consumed in the oxidation of one mole chloride to chlorate in the case of alkali and alkaline earth metal respectively. This is said to correspond to a maximum current efficiency of 100%. If all chlorate is formed by reaction (6) the current efficiency cannot be higher than 66.5% since one third of the current is used for the evolution of oxygen. In other words the reaction (6) can be considered as anodic loss reaction. It has been established that the reaction (5) is more plausible than by reaction (6)⁴. The most favorable operating conditions for reaction (5) are a temperature of 333 to 348K with a pH of 6.0 – 6.5.

Under these conditions, a number of subsidiary or parasitic reactions occur, thereby reducing the current efficiency seriously. The main parasitic reactions are the cathodic reduction of hypochlorite and chlorate,



In accordance with the well known chemical properties of these ions, hypochlorite is much more easily reduced than chlorate. Reaction (8) is much slower than chlorate formation, but this reaction plays a negligible role under industrial conditions, unless detrimental corrosion products from anode coating or impregnation are present. In the case of alkaline earth metal chlorides the formation of metal hydroxide will be encountered due to their low solubility. According to M-H₂O Pourbaix diagram¹², hydroxide formation is predicted by the following reaction



$$\log [\text{M}^{2+}] = \log K - 2\text{pH}$$

Where M is magnesium, strontium or barium.

The magnesium, strontium and barium hydroxide forms a layer over the cathode surface and hinder cathodic loss reactions. The above reaction (10) was not possible in the case of alkali metals due to their higher solubility of corresponding metal hydroxides. To study and overcome the cathodic loss reactions and to increase the current efficiency for alkaline earth metal chlorate formation, the effect of chromate on cathodic reaction has been carried out in electrolytes like magnesium, strontium and barium chlorides at 303K and compared with sodium and potassium chloride electrolytes.

Figure 1 shows a typical cyclic voltammograms with a platinum electrode in 2M magnesium chlorate solutions with and without the addition of sodium chromate. From the figure it is observed that the cathodic peak for magnesium chlorate at - 0.20V appear only when sodium chromate is present. This peak is due to the reduction of chromate to Cr (III) was reported elsewhere¹⁰, which in turn forms chromium (III) hydroxide or chromium (III) oxide on the electrode surface. The decrease of current after the peak potential indicates the formation of this chromium (III) hydroxide or chromium (III) oxide film preventing its further growth and the anodic peak in the reverse direction corresponds to the oxidation and thereby the dissolution of the film^{10,11}. The peaks clearly indicate the irreversible nature of the reaction. From the curve (1) of figure 1, it is seen that no reduction peak for chlorate in the absence of chromate has taken place in the cathodic side under these conditions¹².

Figure 2 shows the voltammogram when hypochlorite is present in the sodium chlorate electrolyte. In the absence of chromate (curve 1 of figure 2) a cathodic current for hypochlorite reduction is obtained. When chromate is present in the electrolyte, at different concentrations (curves 2, 3 and 4), the

current for hypochlorite reduction first increases upto -0.4V after which it decreases and finally reaching zero current. It is clear from the figure 1 that the cathodic current starts decreasing at the potential at which the reduction of chromate takes place. In the anodic direction at $+0.60\text{V}$ hypochlorite reduction again takes place. This indicates that the inhibiting chromium (III) hydroxide or chromium (III) oxide layer has disappeared (figure 1), because the chromium hydroxide layer has dissolved electrochemically at that potential, thus allowing hypochlorite reduction. Curve (5) of figure 2 shows the voltammograms of hypochlorite of higher concentration (1.5 g/l) in the electrolyte. The curve obtained is similar to that of curves, 3 and 4 of figure 2 (i.e.) initially hypochlorite reduction current increases after which it decreases and finally reaching zero current.

Figure 3 shows the voltammogram when hypochlorite (0.5, 1.0 and 1.5g/l) is present in the magnesium chlorate electrolyte. From the figure 3, it was found that no hypochlorite reduction peak was observed even in the absence of chromate. This is due to the formation of $\text{Mg}(\text{OH})_2$ on the electrode surface, which is a less efficient alternative to chromate addition in the chlorate production process. The same trend was observed in the case of strontium and barium chlorate electrolytes also.

Figure 4 show the effect of the sweep rate for the reduction of hypochlorite of concentration of 1.0g/l. The deviation with different sweep rates is due to the continuous consumption of hypochlorite in the homogeneous chlorate formation reaction, which lowers the hypochlorite concentration between successive runs¹⁰.

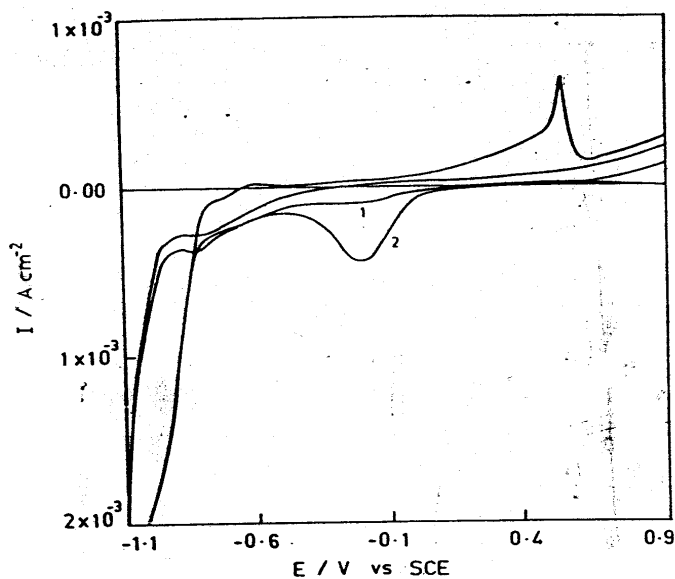


Figure-1

Cyclic voltammogram for magnesium chlorate electrolyte at 338K and at pH 6 with a sweep rate of 50mv s^{-1} and rotation speed of 2000rpm . 1. Background without chromate 2. With 2g l^{-1} chromate

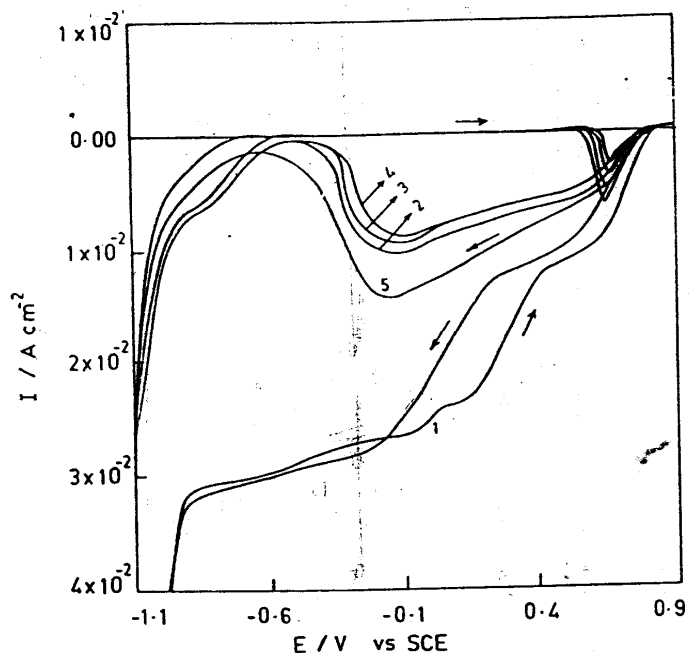


Figure-2

Cyclic voltammogram for sodium chlorate electrolyte with 1.0g/l of hypochlorite at 338K and at $\text{pH}6$ with a sweep rate of 50mv.s^{-1} . 1. without chromate, 2. 1.0g/l of chromate, 3. 2g/l of chromate, 4. 3g/l of chromate, 5. 1.5g/l of hypochlorite

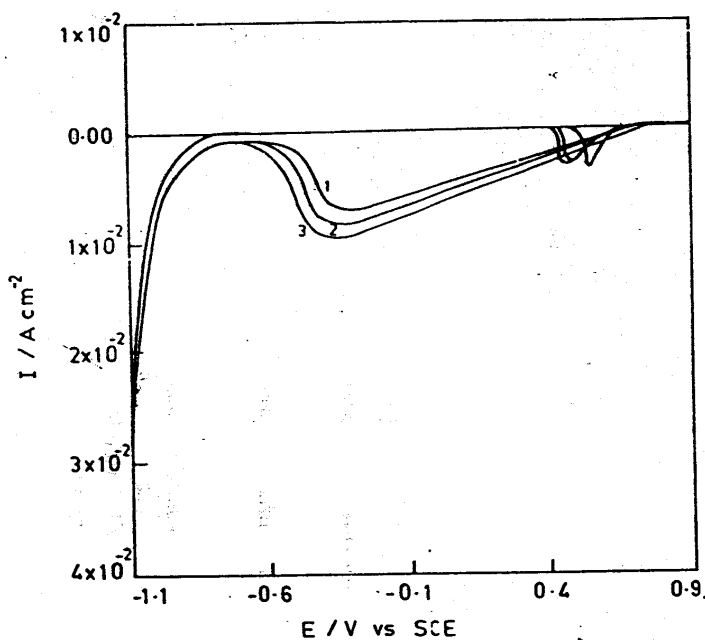


Figure-3

Cyclic Voltammogram for magnesium chlorate electrolyte at 338K and at $\text{pH}6$ with a sweep rate of 50mv s^{-1} . 1. 0.5g/l of hypochlorite, 2. 1.0g/l of hypochlorite and 3. 1.5g/l of hypochlorite

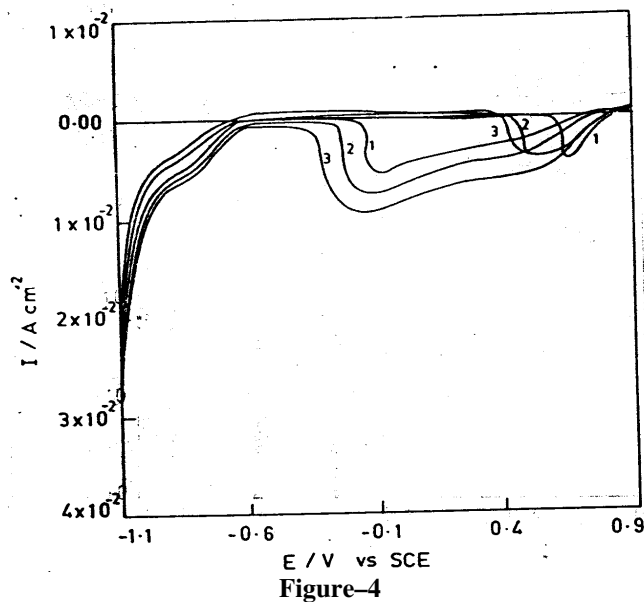


Figure-4
Cyclic Voltammogram for magnesium chlorate electrolyte at 338 K and at pH 6 with 0.5 g/l of hypochlorite, 1. 100 mv s⁻¹, 150 mv s⁻¹ and 200 mv s⁻¹

It is reported¹³ that the suppression of hypochlorite reduction is more effective when chromate is used as addition agent, even though the thickness of chromium hydroxide film is six orders of magnitude thinner than Ca(OH)₂ film (when calcium salt is used as addition agent). But a porous film of alkaline earth metal hydroxides could be an interesting alternative to chromate addition. Hence, in the case of preparation of alkaline earth metal chlorates, the cathodes become covered with alkaline earth metal hydroxide layer due to the precipitation of M²⁺ (where M = Mg, Ca, Sr or Ba) ions with OH⁻ ions due to their low solubility. For example, according to Mg-H₂O Pourbaix diagram¹⁴, magnesium hydroxide formation is predicted by,

$$\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg}(\text{OH})_2 \quad (11)$$

$$\log [\text{Mg}^{2+}] = \log K - 2\text{pH} \quad (12)$$

This visible layer gives further practical support to the popular concept of a “diaphragm” in the technology of chlorate production in the case of alkaline earth metals.

Hence, from these studies it is concluded that the addition of chromate to the electrolyte in the sodium chlorate process suppresses the hypochlorite reduction by forming a thin layer of chromium hydroxide on the electrode surface, and in the case of alkaline earth metal chlorates, the formation of metal hydroxide on the electrode surface suppresses the hypochlorite reduction. It is confirmed that, the higher current efficiencies were achieved in our lab scale and pilot scale studies for the electrochemical preparation of chlorates, bromates and perchlorate¹⁵⁻²⁵ without the addition of any chromate.

Conclusion

It is concluded that, in the case of sodium chlorate electrolyte, the addition of chromate suppresses the hypochlorite reduction

by forming a thin layer of chromium hydroxide on the electrode surface, which prevents the hypochlorite reduction. In the case of magnesium, strontium and barium chlorates, the cathodes become covered with metal hydroxide, which will act as a porous film and prevent the hypochlorite reduction on the cathode surface, which can avoid the addition of chromate to the electrolyte making the chlorate process eco friendly.

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References

1. Wagner C., The Cathodic Reduction of Anions and the Anodic Oxidation of Cations, *J. Electrochem. Soc.*, **101**, 181- 185 (1954)
2. Tilak B.V., Viswanathan K., and Rader C.G., On the mechanism of sodium chlorate formation, *J. Electrochem. Soc.*, **128**, 1228-1232 (1981)
3. Jaksic M.M., Nikolic B.Z., Karanovic, D.M. and Milovanovic C.R., Studies on chlorate cell process, *J. Electrochem. Soc.*, **116**, 394-398 (1969)
4. Vogt H., Balej J., Bennett J., Wintzer P., Akbar Sheikh S., Gallone P., Vasudevan S. and Pelin K., Chlorine Oxides and Chlorine Oxygen Acids, Ullmann's Encyclopedia of Industrial Chemistry, Electronic Release, Wiley-VCH, Weinheim (2010)
5. Kolthoff I.M., Shams A.M. and Din E.I., Reduction of hexavalent chromium at the rotated platinum electrode, Permeability of film formed, *J. Phys. Chem.*, **60**, 1564-1567 (1956)
6. Taniguchi I. and Sekine T., The influence of chromate addition on the cathodic reduction of hypochlorite ion, *Denki Kagaku* **43**, 201-204 (1975)
7. Taniguchi I., and Sekine T., Cathodic reduction of chromate in alkaline solution, *Denki Kagaku*, **43**, 632-635 (1975)
8. Lindbergn G. and Simonsson D., *Electrochimica Acta.*, Inhibition of cathode reactions in sodium hydroxide solution containing chromate, **67**, 1985-1994 (1991)
9. Veselovskya I.E., Kuchinskii E.M. and Morochko L.V., On the mechanism of perchlorate formation, *Zh. Prikl. Khim.*, **37**, 76-62 (1964)
10. Lindbergn G. and Simonsson D., The effect of chromate addition on cathodic reduction of hypochlorite in hydroxide and chlorate solutions, *J. Electrochem. Soc.*, **137**, 3094-3099 (1990)
11. Kelsall G.H., House C.I., and Gudyanga F.P., Chemical and electrochemical equilibria and kinetics in aqueous Cr

- (III)/Cr (IV)chloride solutions, *J.Electroanal.Chem.*, **244**, 179-201 (1988)
12. Hine F. and Yasuda M., On the cathodic reaction in solution containing ClO_3^- , *J.Electrochem.Soc.*, **118**, 182-183 (1971)
 13. Cornell A., Lindbergn G., and Simonsson D., The effect of addition of chromate on the hydrogen evolution reaction and on iron oxidation in hydroxide and chlorate solutions, *Electrochimica Acta*, **37**, 1873-1881 (1992)
 14. Vanmuylder J. and Pourbaix M., *In Atlas of Electrochemical Equilibria in Aquous Solutions: Magnesium*: Vanmuylder, J.; Pourbaix, M., Ed.; Pergamon, New York, 139 (1966)
 15. Pushpavanam S., Mohan S., Vasudevan S., Ravichandran S. and Narasimham K.C., Magnesium chlorate by electrolysis of magnesium chloride, *Bull.Electrochem.*, **6**, 422 – 423 (1990)
 16. Pushpavanam S., Mohan S., Vasudevan S., Ravichandran S. and Narasimham K.C., Electrolytic preparation of magnesium chlorate, *Bull. Electrochem.*, **5**, 364-369 (1989)
 17. Vasudevan S., Mohan S., Pushpavanam S. and Narasimham K.C., Electrolytic preparation of magnesium perchlorate, *J. Appl. Electrochem.*, **22**, 877–882 (1992)
 18. Vasudevan S., Pushpavanam S., Mohan S. and Narasimham K.C., Electrolytic Preparation of magnesium chlorate from magnesium chloride, *J.Appl.Electrochem.*, **22**, 1201–1204 (1992)
 19. Vasudevan S., Mohan S., Pushpavanam S. and Narasimham K.C., Chlorate and perchlorate of strontium by electrolysis, *Bull. Electrochem.*, **9**, 693-694 (1993)
 20. Vasudevan S. and Mohan S. Electrochemical Preparation of Barium Chlorate from Barium Chloride, *Ind.Eng.Chem.Res.*, **45**, 2923-2928 (2006)
 21. Vasudevan S. and Mohan S., Studies on the Electrolytic Preparation of $\text{Ba}(\text{ClO}_4)_2$, *Ind. Eng. Chem. Res.*, **46**, 6211-6216 (2007)
 22. Vasudevan S., Optimization of the Process Parameters for an Electrochemical Preparation of Strontium Perchlorate, *Korean J. Chem. Eng.*, **26**, 1246-1251 (2009)
 23. Vasudevan S., Effect of Cations of Alkali and Alkaline-Earth metal Chlorides for Chlorine, *Ind.Eng.Chem.Res.*, **47**, 976-979 (2008)
 24. Vasudevan S., Studies Relating to Electrolytic Preparation of Potassium Bromate, *Ind.Eng.Chem.Res.*, **47**, 1743 -1746 (2008)
 25. Vasudevan S., Studies relating to cathodic reactions in neutral chloride solutions used in chlorate processes, *Ind. Eng. Chem. Res.*, **47**, 5742-5745 (2008)