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Conference Paper**Effect of Some Anions on the Chlorate Cell Process****M. M. Jakšić, A. R. Despić, B. Ž. Nikolić, and S. M. Maksić**Institute of Chemistry, Technology and Metallurgy, Electrochemistry Department,
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The effect of some non-corresponding ionic species on the anodic process in the chlorate producing electrolytic cells has been investigated. It was shown that increasing concentration of anions such as chromate, nitrate and phosphate results in an increase in the oxygen evolution rate. The effect exhibits an asymptotic tendency at higher concentrations. The resemblance of the curve with the adsorption isotherm suggests anion adsorption and its catalytic effect on charge transfer as a possible cause of increasing electrochemical oxidation of available chlorine. The latter results in a corresponding decrease of the current efficiency of chlorate production. Hence, in spite of the beneficial effect of buffering by some of the anions on the chemical conversion of available chlorine into chlorate, the non-corresponding anion concentrations should be kept as low as possible.

INTRODUCTION

The presence of some non-corresponding anions (CrO_4^{2-} , SO_4^{2-} , CO_3^{2-} , F^-) is characteristic of the electrolyte for the chlorate cell process. At the end of the last century, Müller¹ introduced dichromate addition to the electrolyte in the industrial chlorate production to suppress cathode hypochlorite reduction and to achieve a suitable pH buffering effect for the available chlorine conversion to chlorate as well as for the inhibition of the corrosion of the iron parts of the cell. However, a possible effect of dichromate ions on the anode process in chlorate cells has not been fully elucidated so far. Hence, the aim of the present work was to investigate the effect of some buffering and non-buffering anions on the anodic process in the chlorate cell with platinum and ruthenium oxide coated titanium (DSA) anodes².

EXPERIMENTAL

Apparatus for the investigation of the effect of anionic species on the anodic process in the chlorate cell has already been described elsewhere³. The system consisted of an electrolytic cell and a holding vessel — reactor, which were connected in a loop for the recirculation of the electrolyte. A modified automatic titrator served as a pH-stat, enabling the pH to be maintained constant within ± 0.1 . All measurements were carried out at a constant flow rate (6.0×10^{-4} l/h) and

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current density (2.96 A/dm^2). The cell temperature was 25.0°C , while that in the holding volume was 50.0°C .

Thus, conditions of industrial chlorate production were simulated in the laboratory. The effects have been investigated of the addition of dichromate, phosphate, nitrate, sulphate and fluoride anions on the anodic oxygen evolution and current efficiency of chlorate production. The electrolyte contained 310 g/l of sodium chloride and 1 g/l ($3.8 \times 10^{-3} \text{ M}$) of sodium dichromate, other additives being varied from $1 - 20 \times 10^{-2} \text{ M}$.

The results are shown in Fig. 1. It is seen that the increase of dichromate, phosphate and nitrate ion concentrations exhibits a profound effect on oxygen

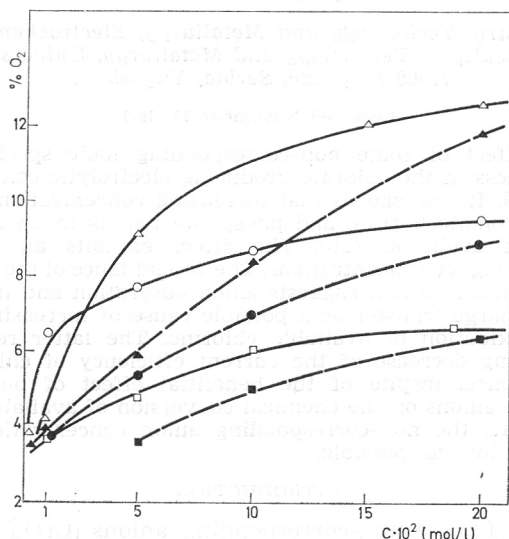


Fig. 1. The influence of some anions on the rate of oxygen evolution in the chlorate cell process on platinum (Δ , \circ , \square) and a DSA-anode (\blacktriangle , \bullet , \blacksquare). The symbols pertain to the $\text{Cr}_2\text{O}_4^{2-}$, PO_4^{3-} , and NO_3^- anions respectively and C is the anion concentration.

evolution rate. For both investigated electrodes this is asymptotic to some limiting value at higher concentrations.

One should note, however, that at comparable current densities in the low concentration region the DSA electrode exhibits considerably lower oxygen evolution rates than the platinum electrode.

Phosphate and nitrate anions exhibit quite similar but significantly smaller effect on oxygen evolution.

Sulphate and fluoride have practically no effect on the anodic chlorate process.

Fig. 2 shows the overall current efficiency (t_1) in the chlorate cell as a function of the above anionic species, which in effect reflects the results and conclusions arising from the previous figure. The current efficiency is known to be³

$$t_1 = \frac{(1 - 2Q - 3S)(1 - P)}{(1 - Q - S)} \quad (1)$$

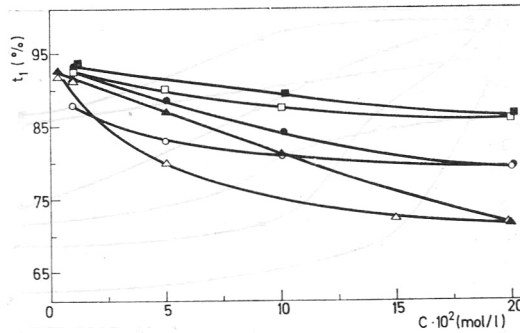


Fig. 2. The influence of the investigated anions on the current efficiency (t_1) in the chlorate cell process. Symbols are the same as those in Fig. 1.

where Q and S are the chlorine and oxygen concentrations in the gas respectively, and P is the loss due to cathodic reduction. Hence, increasing and leveling-off S leads to decreasing and correspondingly leveling-off of t_1 .

Fig. 3 shows the attainable available chlorine concentrations in the cell as a function of the concentration of added anions.

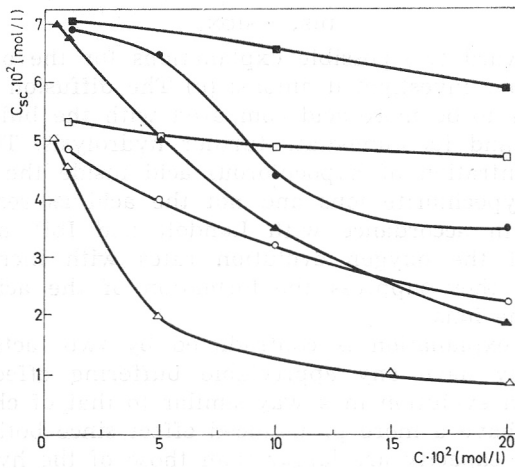
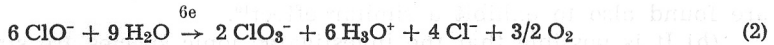


Fig. 3. The steady-state concentration of available chlorine in the chlorate cell (C_{se}) as a function of concentrations of the investigated anions (C). Symbols are the same as those in Fig. 1.

The Foerster equation for the anodic formation of chlorate⁴



gives the stoichiometric relationship between the amount of disappearing available chlorine and the amount of evolved oxygen. Additional oxygen, can, of course, be evolved simultaneously and independently of the chlorate process from the oxydation of water. Our experimental results show, however, a corresponding decrease in the available chlorine content proportional to the intensity of anodic oxygen evolution.

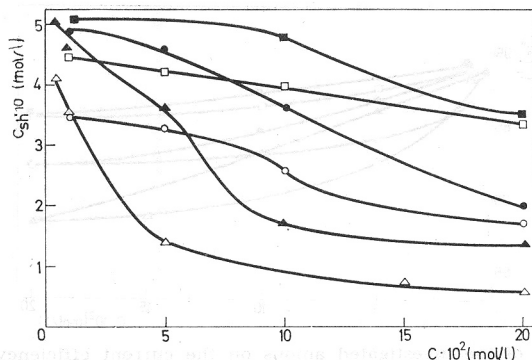


Fig. 4. The steady-state concentration of available chlorine inside the holding vessel (C_{sh}) as a function of concentrations of the investigated anions (C). Symbols are the same as those in Fig. 1.

Fig. 4 shows the available chlorine concentration in the holding volume. Since that is primarily a function of the available chlorine concentration in the incoming solution from the cell, these results are a logical consequence of the ones previously shown.

DISCUSSION

One could forward two possible explanations for the observed effect of dichromate and other investigated anions: (a) The diffusion layer in vicinity of the anode, tends to be more acid compared with the bulk because of the chlorine evolution and its immediate further hydrolysis. The latter creates an increased concentration of hypochlorous acid inside the boundary layer. If one considers hypochlorite ions and not the acid as responsible for the oxygen evolution, in accordance with Landolt and Ibl⁵, one could expect further increase of the oxygen evolution rates with increasing buffering ions content, since they suppress the formation of the acid and stimulate the formation of the ions.

However, this explanation is contradicted by two facts: (i) the nitrate ions cannot possibly have any appreciable buffering effect and yet they do influence oxygen evolution in a way similar to that of chromates; (ii) the phosphates should have a more pronounced effect since both their pK value and their buffering capacity are larger than those of the hydrochromic acid.

The observed effect of those anions, however, is smaller than that of chromate.

Recently it was found⁸ that perchlorate ions with no buffering capacity whatsoever, also cause increase in oxygen evolution rate proportional to their concentration (cf.⁹). Although with different power the molybdate ions are found also to exhibit a similar effect¹⁰.

(b) It is possible that the investigated ionic species are strongly adsorbed at the positive potentials in the anode double layer and hence disturb the normal double layer structure and make the electrode surface more easily accessible for the available chlorine oxidation or catalyze the electron transfer. This conclusion is supported by the fact that each ionic species exhibits a specific effect and yet similar to that exhibited by others, and also by the fact that the shape of the concentration dependence resembles an

adsorption isotherm. The limiting rate of oxygen evolution could reflect the attaining of full surface coverage by these anions. A further support can be found in the fact that the effect is potential dependent in the right direction. That is: the anion adsorption should be less at the less positive potentials at which the DSA electrode operates, and indeed the effect on oxygen evolution rate is smaller.

This is not an entirely new idea. Phillipov, Eberil, Agapova, and Razygraeva⁶ showed that the graphite wear in chlorate process is linear with sodium chromate content up to 30 g/l, above which there is no further increase of the effect. A similar effect, but much less pronounced is observed by these authors, on the oxygen evolution rate and current efficiency.

Eberil⁷ considered adsorption of chromate in the anode double layer as a possible cause of the increased graphite wear and oxygen evolution rate.

One could argue that the increasing oxygen evolution rate comes from an increasing participation of the oxygen evolved by the direct oxidation of water molecules. However, in such a case the Foerster equation (Eq. (2)) could not be obeyed, and there could be no straight forward relationship between the oxygen evolution rate and the available chlorine concentration.

In an earlier work³ it was shown that the current efficiency in chlorate electrolysis is given by the equation

$$t_1 - \frac{2}{3} = \frac{2}{3} F \cdot \left(\frac{q}{I} \right) \cdot (C_{sc} - C_{sh}) \quad (3)$$

where q represents the flow rate, F — Faraday constant, I — the total current or the cell load, C_{sc} and C_{sh} — the available chlorine concentrations coming out and into the cell, respectively. This equation is a direct consequence of the application of the Foerster stoichiometry and has been proved valid by many experiments reported in our earlier work³.

Fig. 5 shows that this equation proves valid also in the new experiments with the various anionic species investigated.

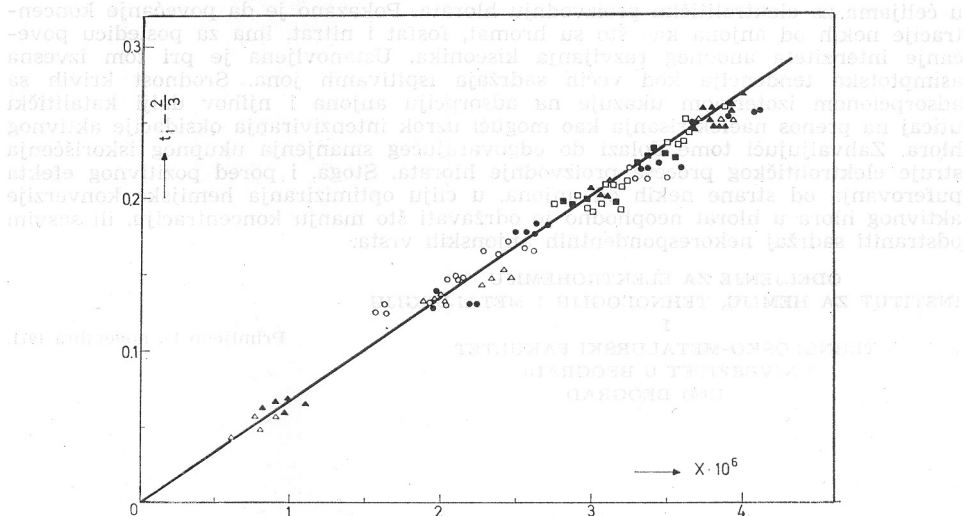


Fig. 5. The test of the equation (3) for the effect of the chemical conversion of available chlorine in the holding vessel [$X = (q/I) \cdot (C_{sc} - C_{sh})$]. The solid line represents the theoretical result.

A practical conclusion can also be drawn from the above results:

In the industrial chlorate cell process one should limit the dichromate content to avoid undue current losses, inspite of the fact that its buffering effect increases with its concentration and thus helps chemical conversion of available chlorine to chlorate.

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IZVOD

Uticaj izvesnih anjona na elektrolitički proces proizvodnje hlorata

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Ispitan je uticaj izvesnih nekorespondentnih anjonskih vrsta na anodni proces u ćelijama za elektrolitičku proizvodnju hlorata. Pokazano je da povećanje koncentracije nekih od anjona kao što su hromat, fosfat i nitrat, ima za posledicu povećanje intenziteta anodnog razvijanja kiseonika. Ustanovljena je pri tom izvesna asimptotska tendencija kod većih sadržaja ispitivanih jona. Srodnost krivih sa adsorpcionom izotermom ukazuje na adsorpciju anjona i njihov dalji katalitički uticaj na prenos naelektrisanja kao mogući uzrok intenziviranja oksidacije aktivnog hlorata. Zahvaljujući tome dolazi do odgovarajućeg smanjenja ukupnog iskorišćenja struje elektrolitičkog procesa proizvodnje hlorata. Stoga, i pored pozitivnog efekta puferovanja od strane nekih od anjona, u cilju optimiziranja hemijske konverzije aktivnog hlorata u hlorat neophodno je održavati što manju koncentraciju, ili sasvim odstraniti sadržaj nekorespondentnih anjonskih vrsta.

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