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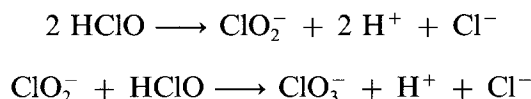
Formation of hypochlorite, chlorate and oxygen during NaCl electrolysis from alkaline solutions at an RuO₂/TiO₂ anode

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On-site electrolysis of a weak alkaline solution of NaCl has been applied to an increasing extent for disinfection. To optimize the electrolytic cell and the electrolysis conditions, the current efficiency for hypochlorite, chlorate and oxygen formation at a commercial RuO₂/TiO₂ anode were determined under various conditions. It was found that for solution with low NaCl concentrations, (lower than 200 mol m⁻³), and at 298 K, solution flow velocity of 0.075 m s⁻¹ and high current density, (higher than 2 kA m⁻²), hypochlorite formation is determined by mass transfer of chloride. The formation of chlorate in weakly alkaline media at a chlorine and oxygen-evolving anode is ascribed to two reactions, namely, the direct oxidation of chloride to chlorate and the conversion of hypochlorite. This is suggested to split the well-known electrochemical Foerster reaction into a chemical reaction for the conversion of hypochlorite in chlorate and the electrochemical oxidation reaction of water. It is proposed that in an acidic reaction layer at the anode the mechanism of chlorate formation may be given by the following:



Notation

A_e electrode surface area (m²)
 c_i concentration of species i (mol m⁻³)
 $c_{i,0}$ c_i at $t_e = 0$ (mol m⁻³)
 D_i diffusion constant of species i (m² s⁻¹)
 E electrode potential versus saturated calomel electrode (V)
 F Faraday constant (C mol⁻¹)
 i current (A)
 j current density (A m⁻²)
 j_d diffusion-limiting current density (A m⁻²)
 h_i slope of n_i/c_3 curve (m³ s⁻¹)
 $k_{d,i}$ diffusion mass-transfer coefficient of species i (m s⁻¹)
 $k_{d,f,i}$ $k_{d,i}$ at forced convection of solution and in the absence of bubble (m s⁻¹) evolution
 N_i quantity of species i formed during the electrolysis (mol)
 n_i rate of formation for species i (mol s⁻¹)
 $n_{4,g}$ n_4 determined by diffusion limitation of hypochlorite (mol s⁻¹)
 t time (s)
 t_e time of electrolysis (s)
 T absolute temperature (K)

v_0 average flow velocity of solution in the anodic compartment of the cell at the level of the leading edge of the electrode (m s⁻¹)
 ϕ_i current efficiency for species i
 $\phi_{i,0}$ ϕ_i at $t_e = 0$

Subscripts

av average
d diffusion
e electrolysis, electrode
f forced convection
ox oxygen

The numbers 1, 2, 3 and 4 are used according to the scheme set out in the table (below).

Ionic species	Cl ⁻	Cl ₂	ClO ⁻	ClO ₃ ⁻
Concentration (mol m ⁻³)	c_1	c_2	c_3	c_4
Formation rate (mol s ⁻¹)		n_2	n_3	n_4
Quantity of product formed (mol)		N_2	N_3	N_4
Current efficiency		ϕ_2	ϕ_3	ϕ_4
Diffusion mass transfer coefficient (m s ⁻¹)	$k_{d,1}$		$k_{d,3}$	

1. Introduction

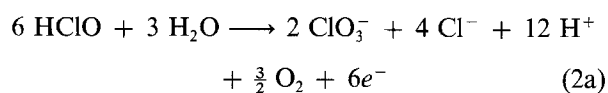
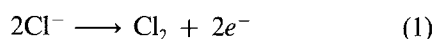
Hypochlorite is used for disinfection of drinking water and process equipment in the food and beverage industries. The interest in on-site generation has grown during the last decades. Comprehensive review articles on hypochlorite and chlorate formation by electrolysis of a sodium chloride solution have been published by Ibl and Vogt [1] and more recently by Novak, Tilak and Conway [2].

The competitive generation of oxygen, chlorine, hypochlorite and chlorate has never been examined simultaneously. Chlorate is formed by anodic oxidation of hypochlorite and/or by chemical conversion of hypochlorite ion and hypochlorous acid. Generally, the Foerster reaction [1] is accepted for the anodic formation of chlorate. Several authors have proposed various reaction schemes, where the stoichiometry of the anodic formation of chlorate deviates from that for the Foerster reaction [1].

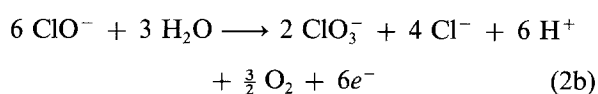
Previously the anodic formation of chlorate was studied with graphite and platinum electrodes. During the last ten years, a new anode material, particularly (RuO₂ + TiO₂)-based coatings on Ti-substrate (DSA[®] electrodes) has been used to an increasing extent for the electrochemical production of hypochlorite and chlorate. To elucidate the anodic reactions, current efficiency experiments were carried out in a divided cell with an industrial DSA[®], in which the current density and the composition of anolyte were varied.

2. Reactions at the anode and in the anolyte

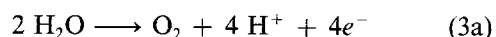
For the electrolysis of slightly acidic NaCl solutions the main reactions at the anode are [1]:



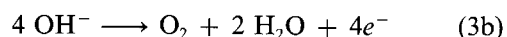
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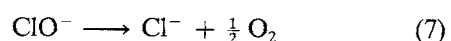
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or



and the main reactions at the anolyte are



For the electrochemical formation of chlorate, some

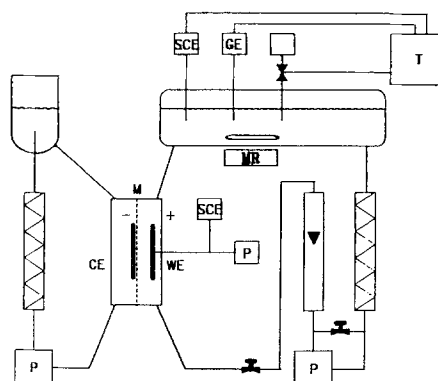


Fig. 1. Experimental set-up. WE: working electrode (anode), CE: counter electrode (cathode), M: membrane, SCE: saturated calomel electrode, GE: glass electrode, T: titrator, MR: magnetic stirrer, P: pump.

investigators have suggested other reactions [1] for which the ratio between the number of ClO₃⁻ ions or HClO₃ molecules and the number of ClO⁻ ions or HClO molecules varies between 0.5 and 1.0. This ratio is 0.33 for Reactions 2a and b, which are well-known as the Foerster reactions.

3. Experimental details

3.1. Equipment and experimental conditions

The experimental set-up with two separate circuits of solution, the anodic and the cathodic circuit, is schematically shown in Fig. 1. The acrylate electrolysis cell, was divided by a cation-exchange membrane (Nafion 117) into an anodic and a cathodic compartment.

The thermostated solutions in both circuits were pumped upwards through the cell. The anodic circuit contained a large overflow vessel of about 3000 cm³ and the cathodic circuit a small one. A flowmeter (Fischer and Porter 3F-3/8-25-5/56 with a tantalum float) was placed only in the anodic circuit. The average velocity in the anodic compartment of the cell at the level of the leading edge of the working-electrode, v_0 , was adjusted to 0.075 m s⁻¹. The rate of flow in the counter-electrode compartment was sufficiently high to prevent accumulation of gas inside the cell.

The working electrode (DSA[®]) was placed against the back wall of the anodic compartment at a distance of 8 mm from the membrane. The working electrode was 76.5 mm in length and 14.2 mm in width. Its geometric surface area was 1086 mm². The counter electrode was a perforated nickel plate with the same geometric dimensions as the working electrode. It was placed in the counter-electrode compartment opposite to the working electrode and pressed against the membrane.

A hole with a diameter of 2.0 mm was located in the middle of the working electrode. A Luggin capillary, placed in this hole, was filled with a NaCl solution of the same concentration as the anolyte at the start of the electrolysis and connected to a saturated calomel

electrode which was used as the reference electrode. In order to prevent the penetration of gas bubbles into the capillary, a reservoir containing NaCl solution was connected to a tube between the capillary and reference electrodes. The sodium chloride solution from the reservoir was pumped continuously with a volumetric rate of $11 \text{ mm}^3 \text{ s}^{-1}$ through the capillary into the anodic compartment.

The electrolyses were carried out galvanostatically using a power supply (Delta Elektronika, type D.050–10). The potential between the working electrode and the reference electrode was registered and this potential was corrected for the ohmic potential drop. All potentials given are referred to the saturated calomel electrode (SCE).

To maintain the pH of the anolyte constant during electrolysis it was necessary to add an alkaline solution to the anolyte. The addition of the titrance, usually a 4 kmol m^{-3} NaOH solution, was regulated by an automatic titrator (Radiometer, type TTTIC), a valve and a burette. Some experiments were carried out at a practically constant concentration of NaCl in the anolyte. In these cases the titrance was a 4 kmol m^{-3} NaOH solution containing NaCl.

To determine the rate of oxygen formation during electrolysis, helium gas (99.99%) was passed over the solution in the overflow vessel in the anodic circuit. Thereafter, the helium gas and the gas formed during the electrolysis were passed through a 1 kmol m^{-3} KOH solution and then through a Hersch cell [3, 4]. To obtain reproducible results, before each series of experiments the Hersch cell was calibrated with an air–helium mixture of a known composition. Since the response of the Hersch cell depends on the flow velocity of the gas, the helium flow for the calibration and the oxygen measurements was always adjusted to $7.1 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The response time of the Hersch cell and the NaCl electrolyser was examined by injection of 50 cm^3 air into the electrolysis cell. A response time of about two minutes was found.

A series of experiments were started with 2000 cm^3 anolyte containing 0.25 to 1.5 kmol m^{-3} sodium chloride and in some experiments, additionally, a known quantity of another anion, for instance hypochlorite, chlorate, perchlorate or sulphate ion. In some experiments a quantity of the appropriate salt was added after an electrolysis time of about 70 min.

A volume of 750 cm^3 of a 1 kmol m^{-3} sodium hydroxide solution served as catholyte. The pH, the temperature and the flow velocity of anolyte were adjusted to 8 or 10, 298 K and 0.075 m s^{-1} , respectively, before starting the electrolysis, and were kept constant during the electrolysis. Generally, solution samples of 10 cm^3 were taken during the electrolysis at intervals of approximately 8 min.

3.2. Analysis of solutions

Many methods have been proposed for the analysis of a solution of chlorine–oxygen compounds [5–8]. Total

analysis methods have the major disadvantage of being time consuming, whereas the measurement of current efficiency at the beginning of the electrolysis requires very short sampling times. The sampling time was reduced to about 8 min by carrying out the determination of the hypochlorite content in the sample immediately after the sampling, whereas the determination of the chlorate content was carried out soon after the completion of the electrolysis. The hypochlorite as well as the chlorate content were determined potentiometrically using the $\text{AsO}_3^{3-}/\text{AsO}_4^{3-}$ redox couple [8].

After the determination of the hypochlorite content in an anolyte sample of 5 cm^3 , the same sample was used to determine the chlorate content. The analysis of samples was carried out in duplicate.

4. Results

4.1. Oxidation products

Chlorine gas, hypochlorite, chlorite, chlorate, perchlorate and oxygen may be the oxidation products formed in the anodic compartment by electrochemical and/or chemical reactions during electrolysis of sodium chloride solutions in the pH range of 7 to 12. We found that the gas leaving the overflow vessel of the anodic compartment contained no chlorine. Consequently, all the chlorine formed at the anode was converted into chlorine–oxygen compounds. Chlorite could not be detected by a potentiometric titration with an arsenite solution. Consequently, the formation of chlorite can be neglected. To investigate the formation of perchlorate, electrolysis of a solution of 0.1 kmol m^{-3} NaCl was carried out with a platinum anode for three hours at a pH of 8, a temperature of 343 K and a current density of 1.91 kA m^{-2} . Subsequently, the electrolysis solution was immediately stabilized by adjusting the pH to 12 and cooling to 273 K. A sample of this solution ($1 \mu\text{l}$) was analysed by means of the technique of isotachopheresis [9, 10] at a pH of 6 using chloride ions in the leading and morpholino-ethane-sulphonic acid in the terminating solution. From the analysis it followed that the formation of perchlorate can be neglected. The detection limit of this analysis for perchlorate is about 0.1 mol m^{-3} corresponding to a current efficiency of about 2%. Since the current efficiency for hypochlorite is higher for a ruthenium dioxide anode than for a platinum anode, it is likely that the formation of perchlorate is of no significance for the ruthenium dioxide anode.

Moreover, we found that practically no chlorate was formed at a pH of 10, a temperature of 343 K and for a hypochlorite concentration of 20 mol m^{-3} .

4.2. Determination of current efficiencies at the start of electrolysis

The total time of electrolysis was kept short, less than one hour, in order to obtain the current efficiencies at

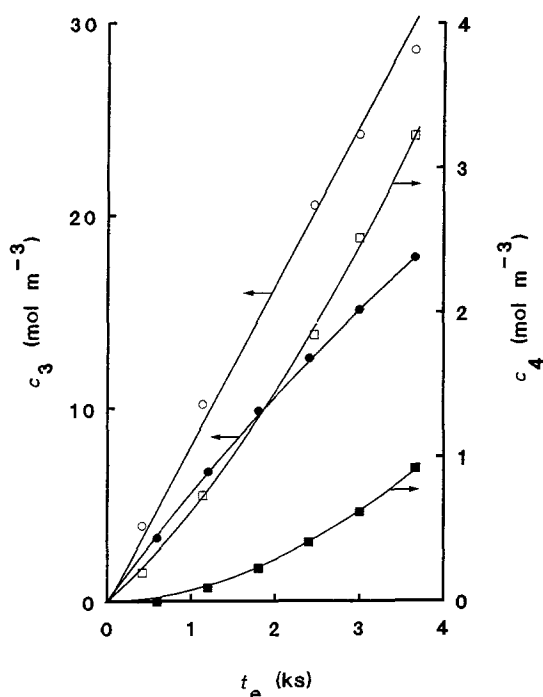


Fig. 2. Plot of hypochlorite and chlorate concentration, respectively c_3 and c_4 against time of electrolysis, t_e , for a ruthenium oxide anode at two different current densities, pH 10 and in a solution with $c_{1,0} = 100 \text{ mol m}^{-3}$, where the pH was kept constant by addition of NaOH solution as titrance. Hypochlorite: (O) 2.76 kA m^{-2} and (●) 5.54 kA m^{-2} ; chlorate: (□) 2.76 kA m^{-2} and (■) 5.54 kA m^{-2} .

the start of the electrolysis without a significant change in the composition of anolyte.

Typical results are shown in Fig. 2. In this figure the hypochlorite and the chlorate concentration, respectively c_3 and c_4 , are plotted versus the time of electrolysis, t_e , for two electrolyses with different current densities, 2.76 and 5.54 kA m^{-2} , and the same initial NaCl concentration, 100 mol m^{-3} . The chloride concentration decreased during the electrolysis from 100 to 83 and 66 mol m^{-3} for, respectively, 2.76 and 5.54 kA m^{-2} after 1 h of electrolysis.

Taking into account the anolyte volume at the start of electrolysis, the volume of NaOH solution added to the anolyte and the volume of water transported from the anodic to the cathodic compartment through the membrane (about $1.8 \mu\text{s}^{-1}$), the total quantities of hypochlorite and chlorate, respectively N_3 and N_4 , present in the anolyte and in the anolyte samples were determined.

The average rate of hypochlorite and chlorate formation, $n_{3,av}$ and $n_{4,av}$ in a period of electrolysis were given by, respectively $\Delta N_3/\Delta t_e$ and $\Delta N_4/\Delta t_e$. It has been found that the most reliable results for $n_{3,0}$ and $n_{4,0}$ were obtained by plotting $n_{3,av}$ and $n_{4,av}$ as a function of the average concentration of hypochlorite $c_{3,av}$ in the selected periods of electrolysis. Figure 3 shows the results for the experiments from Fig. 2.

Linear extrapolation of the declining $n_{3,av}$ against $c_{3,av}$ and of the inclining $n_{4,av}$ against $c_{3,av}$ curves to $c_3 = 0$ give $n_{3,0}$ and $n_{4,0}$, respectively.

The current efficiency of hypochlorite formation is given by

$$\phi_3 = 2Fn_3/A_ej$$

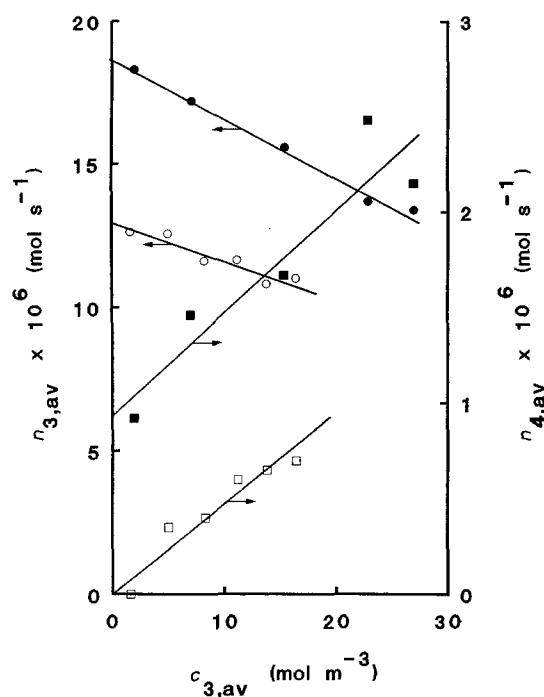


Fig. 3. Average rate of hypochlorite and chlorate formation in selected periods of electrolysis, respectively $n_{3,av}$ and $n_{4,av}$, as a function of the average hypochlorite concentration $c_{3,av}$ in the selected periods of electrolysis. Experimental conditions are given in the subscript of Fig. 2. Hypochlorite: (O) 2.76 kA m^{-2} and (●) 5.54 kA m^{-2} ; chlorate: (□) 2.76 kA m^{-2} and (■) 5.54 kA m^{-2} .

where two electrons are involved in the reaction for the hypochlorite formation, F is the Faraday constant, A_e is the electrode surface area, and j the current density. The current efficiency for the chlorate formation is defined by

$$\phi_4 = 6Fn_4/A_ej$$

where one ClO_3^- ion is formed from three ClO^- ions or from one Cl^- ion.

From Fig. 3 it follows that the initial rate of chlorate formation is practically zero for the lowest current density, that is 2.76 kA m^{-2} and about $0.8 \times 10^{-6} \text{ mol s}^{-1}$ corresponding to a current efficiency $\phi_{4,0} = 0.08$ for the highest current density, that is 5.52 kA m^{-2} . The rate of chlorate formation, n_4 , can be given by $n_4 = n_{4,0} + h_4c_3$ where $n_{4,0}$ and h_4 depend on various parameters, for instance current density and initial concentration of NaCl (Fig. 3).

The rate of oxygen formation was determined using a Hersch cell. Before the start of electrolysis the circuit of anolyte was made practically free of oxygen by passing helium through the overflow vessel during about 30 min. About 2 min after switching on the electrolysis current, an increase in the current of the Hersch cell was observed. From the current of the Hersch cell and its calibration curve, the rate of oxygen formation, n_{ox} , has been calculated. A typical result is given in Fig. 4. From this figure it follows that the increase in n_{ox} is almost linear with increasing hypochlorite concentration. Extrapolation to $c_3 = 0 \text{ mol m}^{-3}$ gives $n_{ox,0}$. The current efficiency for oxygen evolution is calculated by

$$\phi_{ox} = 4Fn_{ox}/A_ej$$

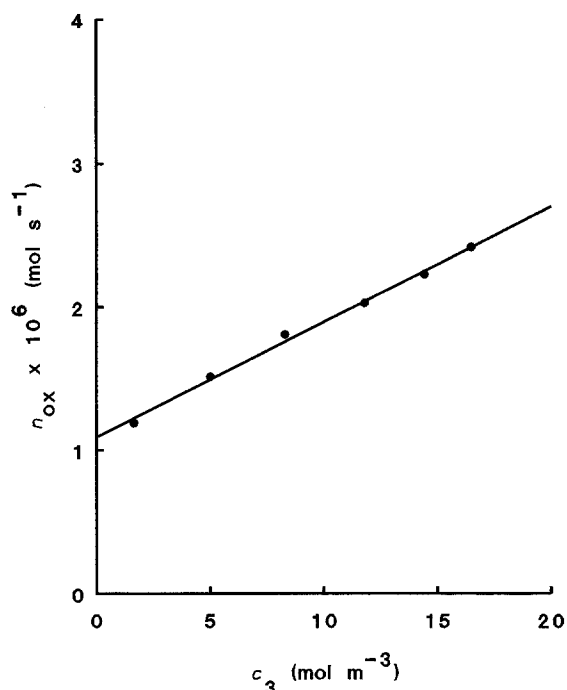


Fig. 4. Rate of oxygen formation as a function of the hypochlorite concentration for an electrolysis at $j = 2.76 \text{ kA m}^{-2}$, pH 10 and at $c_{1,0} = 100 \text{ mol m}^{-3}$. A 4 N NaOH solution was used as the titrance.

From the experimental results it was concluded that the sum of the current efficiencies for hypochlorite, chlorate and oxygen is 1. It should be noted that the Hersch cell is very useful to indicate a change in the rate of oxygen evolution during the electrolysis; however, the stability of the Hersch cell over a long period was rather poor.

To obtain insight into the reproducibility of the experimental results, five experiments were carried out under the same conditions, namely $i = 3 \text{ A}$, $T = 298 \text{ K}$, a solution flow rate of 0.075 m s^{-1} , $c_{1,0} = 100 \text{ mol m}^{-3}$ and a 4 M NaOH solution as the titrance. It was found that $\phi_{3,0} = 0.77 \pm 0.04$, $\phi_{4,0} \approx 0$, and $\phi_{\text{ox},0} = 0.19 \pm 0.04$. The slopes for the three curves n_3 against c_3 , n_4 against c_3 and n_{ox} against c_3 , h_3 , h_4 and h_{ox} , are $-(0.15 \pm 0.02) \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, $(0.05 \pm 0.02) \times 10^{-2} \text{ m}^3 \text{ s}^{-1}$, and $(0.07 \pm 0.01) \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$, respectively.

4.3. Effect of current density

The effect of the current density on the current efficiencies at the beginning of the electrolysis, that is on $\phi_{3,0}$, $\phi_{4,0}$ and $\phi_{\text{ox},0}$, is illustrated in Fig. 5 for experiments with an initial sodium chloride concentration of 100 mol m^{-3} . The average sum of the current efficiencies is 99%. Figure 5 shows that $\phi_{3,0}$ decreases and $\phi_{4,0}$ and $\phi_{\text{ox},0}$ increase with increasing current density. Moreover, the ratio $\phi_{\text{ox},0}/\phi_{4,0}$ increases with increasing current density. The slope h_4 of the n_4/c_3 curve is also given in Fig. 5.

4.4. Effect of initial NaCl concentration

The rate of oxygen formation was not determined in these experiments. Since it was shown that the sum of

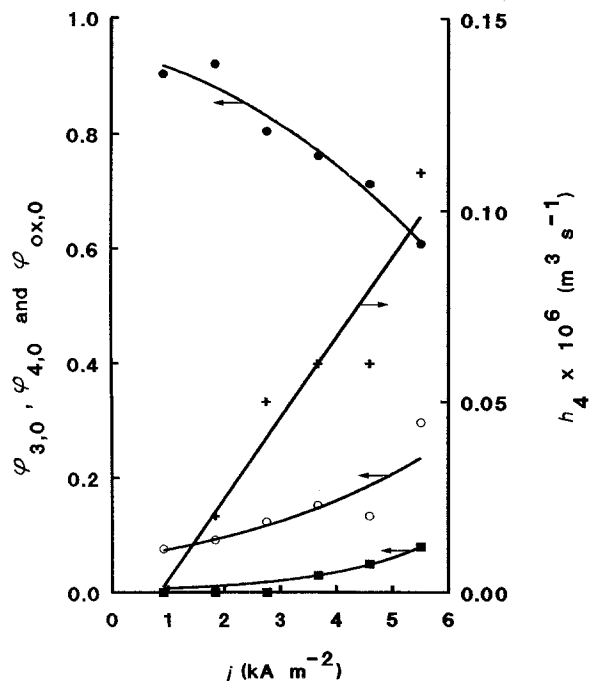


Fig. 5. Effect of the current density on the initial current efficiencies of hypochlorite, chlorate and oxygen and on the slope h_4 of the $n_{4,\text{av}}/c_{3,\text{av}}$ curve at pH 8 and at an initial sodium chloride concentration of 100 mol m^{-3} . (●) $\phi_{3,0}$, (■) $\phi_{4,0}$, (○) $\phi_{\text{ox},0}$ and (+) h_4 .

the current efficiencies for hypochlorite, chlorate and oxygen is about 1.00, the current efficiency of oxygen formation can be calculated from these experiments by $\phi_{\text{ox}} = 1 - \phi_3 - \phi_4$. Figure 6 shows that the concentration of chloride ions clearly affects the current efficiencies. An initial current efficiency of nearly 1.00 is yielded for the electrochemical formation of hypochlorite at NaCl concentration higher

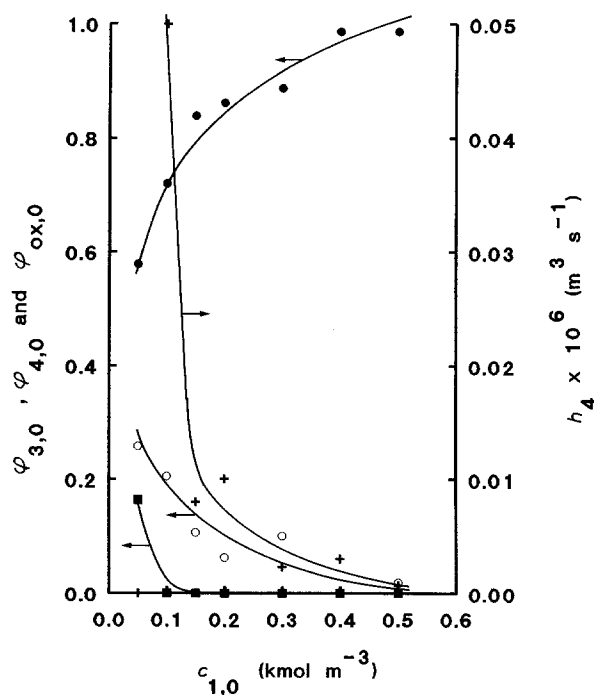


Fig. 6. Effect of the initial sodium chloride concentration on the initial current efficiencies of hypochlorite and oxygen and on the slope h_4 of the $n_{4,\text{av}}/c_{3,\text{av}}$ curve at pH 8 and $j = 2.76 \text{ kA m}^{-2}$. (●) $\phi_{3,0}$, (■) $\phi_{4,0}$, (○) $\phi_{\text{ox},0}$ and (+) h_4 .

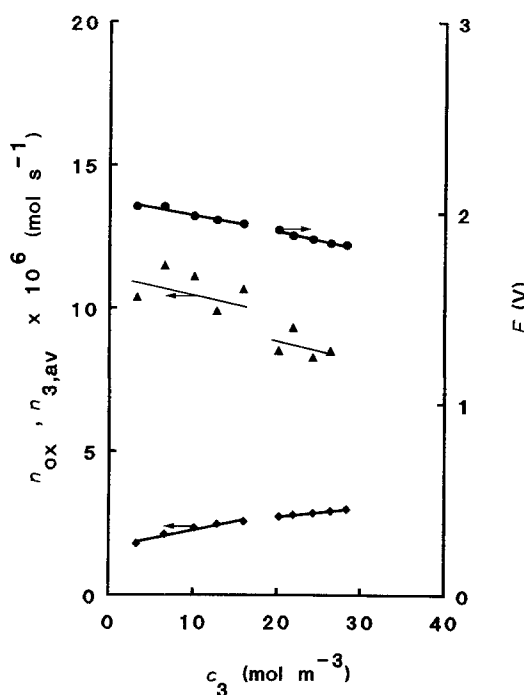


Fig. 7. Effect of the addition of $5 \times 10^{-4} \text{ m}^3$ of 100 mol m^{-3} NaCl on $n_{3,av}$ (\blacktriangle), n_{ox} (\blacklozenge), and anode potential (\bullet) at an electrolysis time of 70 min. The electrolysis was carried out at $j = 2.76 \text{ kA m}^{-2}$, pH 10 and an initial sodium chloride concentration of 100 mol m^{-3} . A $2 \text{ M NaCl} + 4 \text{ M NaOH}$ solution was used as the titrance.

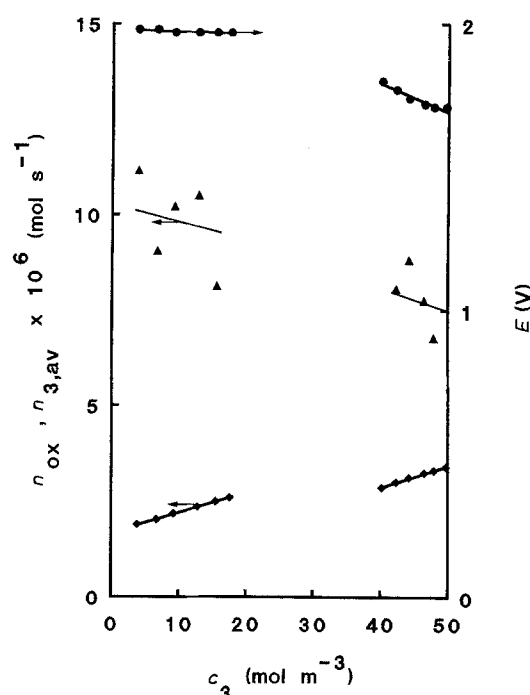


Fig. 8. Effect of the addition of $5 \times 10^{-4} \text{ m}^3$ of 100 mol m^{-3} NaCl + 100 mol m^{-3} NaClO on $n_{3,av}$ (\blacktriangle), n_{ox} (\blacklozenge), and the anode potential (\bullet) at an electrolysis time of 70 min. The electrolysis is carried out at pH 10 and an initial sodium chloride concentration of 100 mol m^{-3} . A $2 \text{ M NaCl} + 4 \text{ M NaOH}$ solution was used as the titrance.

than about 400 mol m^{-3} . The current efficiency for the electrochemical formation of oxygen decreases with increasing initial concentration of NaCl. Figure 6 shows also the slope h_4 ; its accuracy is small.

4.5. Effect of addition of Cl^- , ClO^- and ClO_3^-

The dependence of the formation rates of hypochlorite, chlorate and oxygen on the concentration of chloride, hypochlorite and chlorate ions was investigated by experiments in which one or two of these components were added to the solution after 70 min of electrolysis of a 100 mol m^{-3} NaCl solution at a current density of 2.76 kA m^{-2} . Since the initial concentration of chloride is rather low and the change in the concentration of chloride significantly affects the anodic current efficiencies, the concentration of chloride was held practically constant in these experiments by titration with a sodium hydroxide solution containing sodium chloride instead of a pure sodium hydroxide solution. The ratio of the quantity of hydrogen ions produced to that of chloride ions consumed is about 2:1.

The influence of the anions on the electrolysis is illustrated in Figs 7 to 9 for experiments where after 70 min of electrolysis solutions containing, respectively, 100 mol m^{-3} NaCl, 100 mol m^{-3} NaCl + 100 mol m^{-3} NaClO and 100 mol m^{-3} NaCl + 100 mol m^{-3} NaClO₃, were added.

Hypochlorite solutions were prepared by passing chlorine gas through a solution of 100 mol m^{-3} NaOH. These solutions were diluted and adjusted to the pH used in the electrolysis experiment. Solutions with 100 mol m^{-3} NaCl, 100 mol m^{-3}

NaClO also contained a trace of NaClO₃, that is 0.2 mol m^{-3} NaClO₃.

The addition of a solution containing NaCl or NaCl + NaClO has only a slight effect on n_3 , n_{ox} and anode potential E (Figs 7 and 8). The formation rate of chlorate was also practically not affected by the

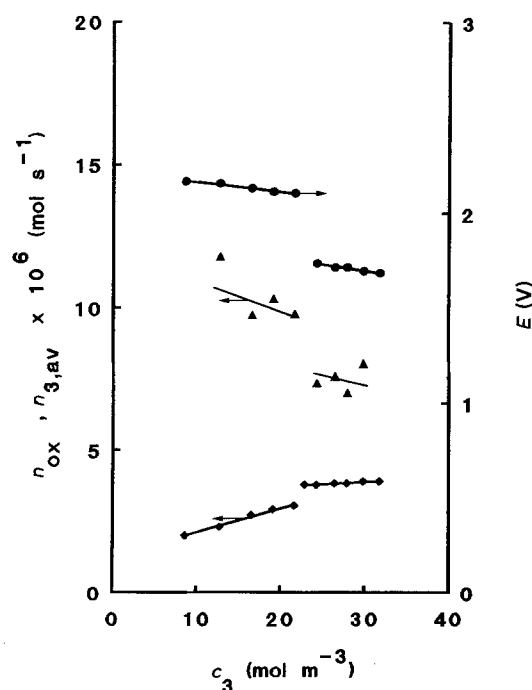


Fig. 9. Effect of the addition of $5 \times 10^{-4} \text{ m}^3$ of 100 mol m^{-3} NaCl + 100 mol m^{-3} NaClO₃ on $n_{3,av}$ (\blacktriangle), n_{ox} (\blacklozenge), and the anode potential (\bullet) at an electrolysis time of 70 min. The electrolysis is carried out at pH 10 and an initial sodium chloride concentration of 100 mol m^{-3} . A $2 \text{ M NaCl} + 4 \text{ M NaOH}$ solution was used as the titrance.

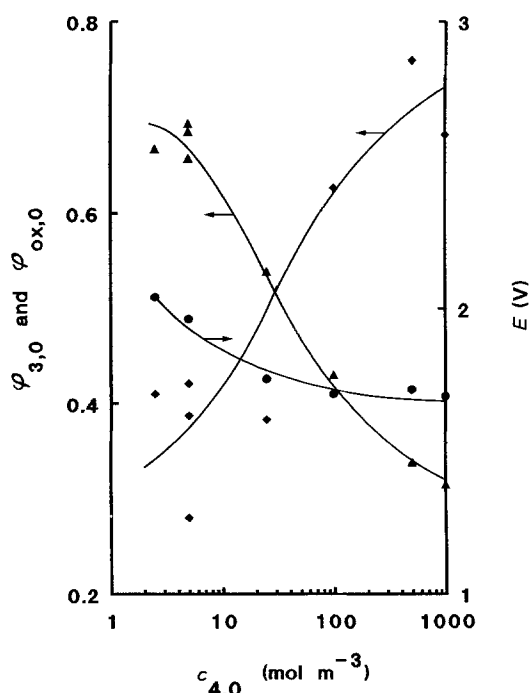


Fig. 10. Effect of the initial chlorate concentration on the initial current efficiencies for hypochlorite (▲) and oxygen (◆) formation and on the initial anode potential (●) for electrolysis with $c_{1,0} = 100 \text{ mol m}^{-3}$ at pH 8 and a current density of 2.76 kA m^{-2} .

addition of the NaCl solution. If the solution containing chloride and hypochlorite was added, the rate of chlorate formation increased with a factor of about 0.3. The addition of chlorate clearly affects the rate of oxygen and hypochlorite formation as well as the anode potential (Fig. 9). Since the chlorate concentration was relatively high after the addition of the chlorate containing solution, reliable results for the rate of chlorate formation were not obtained.

To investigate the effect of NaClO_3 concentration upon $\phi_{3,0}$, $\phi_{ox,0}$ and the anode potential, electrolyses with a solution containing initially 100 mol m^{-3} NaCl and various NaClO_3 concentrations were carried out. The results are shown in Fig. 10. This figure shows that $\phi_{3,0}$ decreases and $\phi_{ox,0}$ increases with increasing $c_{4,0}$. Moreover, $\phi_{3,0}$ at low $c_{4,0}$ is a factor of about 2 higher than at high $c_{4,0}$.

4.6. Effect of perchlorate and sulphate

The effect of the nature of the anion, that is the chlorate, perchlorate and sulphate on the oxygen evolution, was investigated. It was found that for the experiments with 100 mol m^{-3} NaCl containing 25 mol m^{-3} , NaClO_3 , NaClO_4 and Na_2SO_4 and at $j = 2.76 \text{ kA m}^{-2}$ the initial current efficiencies for oxygen formation are 0.38, 0.43 and 0.64, respectively, and the efficiencies for the hypochlorite formation are 0.51, 0.53 and 0.31, respectively.

5. Discussion

5.1. Formation of hypochlorite

The rate of hypochlorite formation depends on the

rate of mass transfer of chloride ions to the anode and/or the kinetic parameters of the electrochemical reactions at the anode. To obtain the diffusion mass transfer coefficient for chloride ions in the absence of gas bubble evolution, the limiting current for the reduction of ClO^- in a solution of 500 mol m^{-3} NaCl + 30 mol m^{-3} NaClO was determined at a solution flow velocity of 0.075 m s^{-1} , pH 10 and at a temperature of 298 K. It was found that the diffusion mass transfer coefficient for ClO^- , $k_{d,f,3}$ is $2.995 \times 10^{-5} \text{ m s}^{-1}$. Taking into account the effect of the difference between the diffusion coefficients for Cl^- and ClO^- ions in water at 298 K, that is between $D_1 = 2.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_3 = 1.51 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, neglecting the small effect of the viscosity of the solution on the ratio of both diffusion coefficients and taking $k_{d,f}$ is proportional to $D^{2/3}$ for laminar flow of solution, it can be calculated that $k_{d,f,1} = 3.65 \times 10^{-5} \text{ m s}^{-1}$ for a 500 mol m^{-3} NaCl solution.

Taking into account the effect of viscosity of solution upon $k_{d,f}$, it can be calculated that $k_{d,f,3} = 3.07 \times 10^{-5} \text{ m s}^{-1}$ and $k_{d,f,1} = 3.74 \times 10^{-5} \text{ m s}^{-1}$ for a 100 mol m^{-3} NaCl solution at 298 K and a solution flow velocity of 0.075 m s^{-1} . From the value of $k_{d,f,1}$ it follows that for the pure NaCl solution with $c_{1,0} = 100 \text{ mol m}^{-3}$ the limiting current density for the chloride oxidation at the DSA[®] electrode in the absence of bubble evolution is 0.72 kA m^{-2} . This agrees well with the current density found for the chloride oxidation at a total current density of 0.90 kA m^{-2} , that is 0.81 kA m^{-2} (Fig. 5). Since for the lowest current density for the series of experiments from Fig. 5 the rate of oxygen evolution is very low, that is 0.09 kA m^{-2} , it can be concluded that even at the lowest current density, 0.90 kA m^{-2} , the oxidation of chloride is determined by its mass transfer to the anode.

When experimental data on the enhancement of mass transfer by oxygen evolution in alkaline solution under conditions of forced convection [11] are used to calculate the diffusion mass transfer coefficient for chloride ions, it follows that the increase in the calculated rate of the diffusion mass transfer of chloride ions with increasing rate of oxygen formation is much smaller than the experimental increase in $k_{d,1}$ determined from the results given in Fig. 5. For instance, the calculated $k_{d,1}$ is $5.84 \times 10^{-5} \text{ m s}^{-1}$ and the experimental $k_{d,1}$ is $17.7 \times 10^{-5} \text{ m s}^{-1}$ for the electrolysis at 5.4 kA m^{-2} (Fig. 5).

Consequently, the chlorine bubble evolution significantly affects the rate of mass transfer of chloride ions to the DSA[®] electrode at high current densities. Moreover, electric heat generation near the anode surface in a NaCl solution with a low NaCl concentration (*i.e.* 100 mol m^{-3}) at a high current density, that is 5.4 kA m^{-2} , may be important for the mass transfer of chloride ions. We conclude that the rate of chloride oxidation is determined by mass transfer of chloride ions for an electrolysis with $c_{1,0} = 100 \text{ mol m}^{-3}$ and $j > 0.90 \text{ kA m}^{-2}$.

Analogously, it can be shown that the rate of

chloride oxidation is determined by mass transfer of chloride ions for an electrolysis at $j = 2.76 \text{ kA m}^{-2}$ and $c_{1,0} \leq 300 \text{ mol m}^{-3}$ and by mass transfer as well as kinetic parameters for an electrolysis at $j = 2.76 \text{ kA m}^{-2}$ and $c_{1,0} > 300 \text{ mol m}^{-3}$.

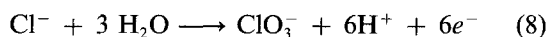
It is well-known that addition of a supporting electrolyte, for instance NaClO_3 , to a NaCl solution results in a smaller limiting current density for the chloride oxidation by reducing the migration current density for chloride ions. From Fig. 10 it follows that $\phi_{3,0}$ at $c_{4,0}$ approaching to zero is a factor of about 2 higher than $\phi_{3,0}$ at a very high $c_{4,0}$. In this case sodium chlorate is used as supporting electrolyte. The factor of 2 is explained by taking into account the contribution of migration of chloride ions to its rate of mass transfer [12].

It can be shown that also the shape of the $\log \phi_{3,0} / \log c_{4,0}$ curve can well be explained by the effect of the chlorate concentration upon migration contribution to the mass transfer for chloride ions [12]. The effect of the nature of the anion upon $\phi_{3,0}$ (Section 4.6) agrees also with this explanation.

5.2. Formation of chlorate

5.2.1. Direct electrochemical oxidation of chloride. The initial rate of chlorate formation depends on the conditions of electrolysis, and is sufficiently high and well determinable for electrolysis experiments with $c_{1,0} = 100 \text{ mol m}^{-3}$ at $j > 2.76 \text{ kA m}^{-2}$ and for those at $j = 2.76 \text{ kA m}^{-2}$ and with $c_{1,0} \leq 300 \text{ mol m}^{-3}$. The ratio between the current density and the initial NaCl concentration determines to a large extent the initial current efficiency for the chlorate formation. Similar results have been observed for a platinum anode [14, 15]. The initial rate of this reaction is, however, much lower for a DSA[®] electrode than for a platinum electrode [14, 15].

The initial rate of chlorate formation has been explained by hydrolysis of molecular chlorine in a reaction layer at the anode [16, 17]. It has been found that both $\phi_{4,0}$ and $\phi_{\text{ox},0}$ increase strongly with decreasing $c_{1,0}$ [14, 15]. Consequently, the initial rate of chlorate formation $\phi_{4,0}$ increases with decreasing pH at the anode, whereas the equilibrium concentration of hypochlorite decreases with decreasing pH [16, 17]. This result does not agree with the model of Ibl and Landolt [16, 17], where the hydrolysis of chlorine determines the initial rate of chlorate formation. We found that $\phi_{4,0}$ increases with increasing current density (Fig. 5) and decreases with increasing initial NaCl concentration (Fig. 6) and, moreover, is affected by the nature of electrode material [14, 15]. These results cannot be well explained by the model of Ibl and Landolt, but agree with a direct electrochemical oxidation of chloride to chlorate without a dissolved hypochlorite species as intermediate. The overall reaction may be



5.2.2. Conversion of hypochlorite. The initial rate of chlorate formation is practically zero for electrolyses with $c_{1,0} = 100 \text{ mol m}^{-3}$ and at $j \leq 2.76 \text{ kA m}^{-2}$ and for those at $j = 2.76 \text{ kA m}^{-2}$ and with $c_{1,0} \geq 300 \text{ mol m}^{-3}$. This means that for these conditions of electrolysis chlorate is completely formed from hypochlorite. This case is discussed next.

Taking into account the Foerster reaction (2 molecules hypochlorite give 1 molecule chlorate) [1] and assuming that the mass transfer of hypochlorite determined by migration and diffusion, the limiting rate of chlorate formation is given by:

$$n_{4,g} = 0.66 k_{d,3} A_e c_3$$

From Fig. 3 it follows that n_4 is $n_{4,0} + h_4 c_3$, so that the slope h_4 is $0.66 k_{d,3} A_e$.

For the electrolysis with $c_{1,0} = 100 \text{ mol m}^{-3}$ and $j = 2.76 \text{ kA m}^{-2}$ the slope h_4 is $5 \times 10^{-8} \text{ m}^3 \text{ s}^{-1}$ (§4.2). Calculation gives $k_{d,3} = 7.0 \times 10^{-5} \text{ m s}^{-1}$. For the same electrolysis it has been calculated that $k_{d,1} = 11.0 \times 10^{-5} \text{ m s}^{-1}$ using $\phi_{3,0} = 0.77$. The ratio $k_{d,1} / k_{d,3} = 1.57$. This ratio agrees reasonably well with the ratio $(D_1/D_3)^{2/3}$ in pure water. Using the reaction scheme presented by Rius and Llopis [18], where the ratio of the stoichiometric number for hypochlorite to that for chlorate is 1.66, it was calculated that $k_{d,3}$ is $3.9 \times 10^{-5} \text{ m s}^{-1}$. This value is much smaller than $k_{d,1}$. Consequently, the reaction scheme presented by Rius and Llopis is unlikely. The same conclusion can be drawn for the scheme given by Shlyapnikov [19], where the stoichiometric ratio is 1.

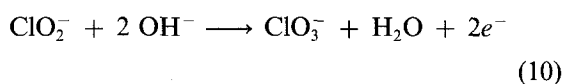
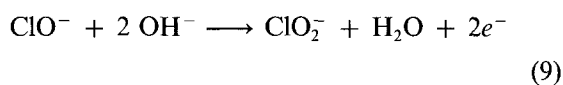
From the preceding discussion it is concluded that the ratio between the stoichiometric numbers for chlorate and hypochlorite is 3.0 as given in the Foerster reaction. Since for the electrolysis with $c_{1,0} = 100 \text{ mol m}^{-3}$ and at $j = 2.76 \text{ kA m}^{-2}$ the initial rate of chlorate formation is zero, it is concluded that in this case the rate of chlorate formation is determined only by diffusion of hypochlorite.

For electrolyses at $j = 2.76 \text{ kA m}^{-2}$ and with $c_{1,0} \geq 300 \text{ mol m}^{-3}$, it can be shown that the rate of chlorate formation as well as the rate of chloride oxidation to chlorine are determined by both mass-transfer and kinetic parameters.

5.2.3. Mechanism of chemical conversion of hypochlorite.

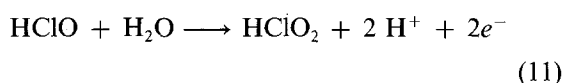
Generally, the Foerster reaction is accepted for describing the electrochemical formation of chlorate from hypochlorite. Considering the Foerster reaction, this reaction can be split into a reaction for the chemical chlorate formation (Reaction 6) and an electrochemical reaction for water oxidation (Reaction 3a). This splitting is only justified if oxygen intermediates are not involved in the mechanism of chlorate formation. The main question is whether oxygen intermediates or hydrogen ions are of crucial interest for chlorate formation. It is well-known that the pH of the solution affects strongly the formation of chlorate from hypochlorite present as hypochlorite ions and/or hypochlorous acid molecules. From current/potential curves at graphite [16]

and at platinum [20] in a NaCl solution of pH = 8 and containing hypochlorite, it has been concluded that hypochlorite and hypochlorous acid molecules are not oxidized at potentials of about 60 mV less positive than the potential where chloride oxidation takes place. Lower pH diminishes the limiting current for hypochlorite oxidation and disappears at and below pH 7 for the bulk of solution [21]. Tasaka and Tojo have suggested [22] that in alkaline solution the anodic oxidation of ClO^- proceeds under the consecutive first order reaction $\text{ClO}^- \rightarrow \text{ClO}_2^- \rightarrow \text{ClO}_3^-$. The proposed reactions are:

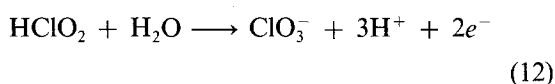


where the rate constant of Equation 9 is much less than the one of Equation 10.

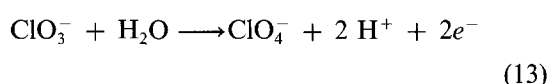
The electrochemical oxidation of hypochlorous acid is difficult to investigate because of its high oxidation potential and the conversion of HClO into Cl_2 . The electrochemical oxidation reaction of HClO and HClO_2 are given by



and



and their standard potentials are 1.405 and 0.97 V/SCE, respectively [23]. A related oxidation reaction, the oxidation of chlorate, has been studied extensively [24]. The electrochemical oxidation of ClO_3^- is



and its standard potential is 0.95 V/SCE.

In practice, oxidation of chlorate to perchlorate occurs at very high electrode potentials, viz. higher than about 1.8 V, and oxygen intermediates are involved in the reaction mechanism [24]. Based on the standard electrode potentials and the high overvoltage for the electrochemical oxidation of ClO_3^- , it is likely that HClO is oxidized at a detectable rate at very high potentials, probably more positive than 1.8 V. This high potential is achieved under extreme conditions of electrolysis, that is a solution with a low concentration of NaCl at very high current densities. Under these conditions the direct electrochemical oxidation from chloride to chlorate has been proposed [14, 15] in the first part of this section and in [14, 15].

In the following, the formation of chlorate during the NaCl electrolysis under more moderate conditions of electrolysis is discussed. The NaCl electrolysis at $j = 2.76 \text{ kA m}^2$, $c_{1,0} = 100 \text{ mol m}^{-3}$ and 298 K, is considered as a characteristic experiment for these conditions. From the rate of oxygen evolution, $1.48 \times$

$10^{-6} \text{ mol s}^{-1}$, and the production of four H^+ ions for each oxygen molecule, using the diffusion mass transfer coefficients and neglecting the consumption of H^+ ions by reactions in the diffusion layer, it can be calculated that the hydrogen ion concentration in the solution at the anode surface is 8.7 mol m^{-3} corresponding to a pH of about 2.0.

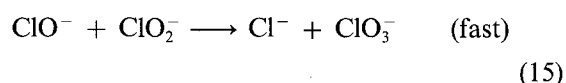
From the constant of ionization for HClO, $2.618 \times 10^{-8} \text{ mol m}^{-3}$ at 298 K [25], it has been calculated that the ratio between the mol fractions of HClO and ClO^- is 0.37×10^6 at pH 2.0 and 298 K. Practically no ClO^- is present at and close to the anode surface. Consequently, the electrochemical oxidation of ClO^- is negligible.

As shown previously, electrochemical oxidation of HClO under moderate conditions of electrolysis is unlikely. This conclusion is supported by the formation of one chlorate ion from three hypochlorite species. If HClO should be electrochemically oxidized, oxygen intermediates would be of great interest and it would be likely that one chlorate ion would be formed from only one hypochlorous acid molecule. The remaining possibility is chemical formation of chlorate from HClO and/or ClO^- .

Various mechanisms for chemical chlorate formation in alkaline and weakly acidic solution have been proposed in the literature [13, 26–30]. The most reliable results are given by Lister [26] for alkaline hypochlorite solutions. The proposed mechanism is given by

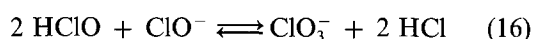


with a rate constant of $0.30 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K, and



In an earlier paper Lister [27] proposed a similar mechanism for the formation of chlorate from hypochlorous acid. However, the experiments were done with an alkaline solution and the experimental rate constant is almost equal to the rate constant of (14); these results are not relevant for chlorate formation from HClO.

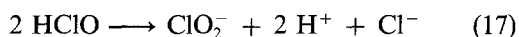
For chemical chlorate formation in weakly alkaline and acidic solution another mechanism was proposed by Foerster [13] and confirmed by other authors [28–30]. This is given by



Using the rate constant given by Tilak *et al.* [30], it can be shown that the experimental rate of chlorate formation cannot take place according to Reactions 14 or 16, since the solution in the diffusion layer is strongly acidic, its pH is about 2. Foerster [13] has stated that the mechanism of chemical chlorate formation and its rate-determining step depend on pH.

Analogously to chlorate formation in alkaline solution, it is likely that a bimolecular reaction of HClO determines the chemical chlorate formation in strongly acidic solution. The proposed reactions are a slow

reaction



and a fast one



Reaction 17 consists of a combination of two uncharged molecules. Its rate constant will be much higher than that of Reaction 14. Therefore, it may be reasonable to assume that chlorate is formed from hypochlorite in a reaction layer with a sufficiently low pH. Since the pH of the reaction layer at the anode is mainly determined by simultaneous formation of H^+ ions and oxygen from water, the rate of chlorate formation will be related to the rate of oxygen during the NaCl electrolysis. Further experimental research is very worthwhile to elucidate the chemical chlorate formation in strongly acidic solution.

5.3. Formation of oxygen

Measurements of oxygen evolution will not elucidate the contribution of Reactions 2 and 6 to the oxygen evolution since both are a source of this element. The rate of oxygen evolution during the electrolysis of this research is determined predominantly by mass transfer of chloride and hypochlorite. A change in the composition of the anolyte, viz. a decrease in NaCl concentration and an increase in the hypochlorite and chlorate concentration affect strongly the mass transfer of Cl^- and ClO^- . Moreover, the presence of a supporting electrolyte diminishes the contribution of migration to mass transfer. This results in a strong increase in the rate of oxygen evolution (§4.5 and §4.6). The oxidation of water is catalysed by the presence of oxygen-containing species as ClO_3^- , ClO_4^- and SO_4^{2-} , since the anode electrode potential declines sharply with increasing concentration of oxygen-containing anions despite the increase of the rate of oxygen evolution (Fig. 10).

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