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Hypochlorite production II. Direct electrolysis in a cell divided by an anionic membrane

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A hypochlorite cell divided by an anionic membrane was examined. The results clearly show that it is possible to suppress cathodic reduction of hypochlorite and to achieve a higher degree of chloride to hypochlorite conversion, at relatively high current efficiencies, than in the case of an undivided cell, using seawater or untreated diluted brine electrolyte.

1. Introduction

Two types of on-site hypochlorite generators [1] are frequently used:

1. Chlorine generation in a miniature chlor-alkali cell incorporating a *cathionic* membrane and using purified brine anolyte. Chlorine gas and caustic solution are continually fed to the water cooled reactor, where the two combine to produce sodium hypochlorite. This type of hypochlorite generation system is capable of producing a solution concentration of 8–15% [2] and is frequently used for disinfection of drinking water and prevention of fouling in heat exchangers [3].

2. Hypochlorite ($HClO + ClO^-$) generation in an undivided cell, in which anodically evolved chlorine is hydrolized in the anode reaction layer using either brine or untreated sea water electrolyte. The electrolyte is pumped through a parallel plate cell at high velocities to give a large volume of low strength NaClO (up to 1%) [4–7]. However, the maximum attainable hypochlorite concentration is limited by loss reactions due to oxidation and reduction. This type of hypochlorite generation system is suitable for prevention of fouling on ships (condenser intakes), etc.

The main characteristics of undivided hypochlorite cells with single pass operation are: low chloride conversion, low efflux hypochlorite concentration and high linear velocity which enables: (i) attainment of relatively high current efficiencies, (ii) reduction of gas locking, (iii) promotion of more uniform current density distribution and (iv) prevention of $Mg(OH)_2$ and $Ca(OH)_2$ film formation at the cathode surface.

The cathodic loss of hypochlorite is a reaction that has to be hindered if a higher performance hypochlorite generator is to be constructed.

The aim of this work was to examine a specially divided cell (incorporating an *anion* selective membrane), in order to achieve a higher degree of chloride to hypochlorite conversion. Relatively higher current efficiencies were expected than in the case of the single pass undivided cell. This should also facilitate the use of untreated sea water or diluted brine electrolyte.

2. Electrochemistry and chemistry of the Cl_2–NaCl–H_2O system

The primary reactions are:

$$\text{Anode:}\quad 2Cl^- \longrightarrow Cl_2 + 2e \tag{1}$$

$$\text{Cathode:}\quad 2H_2O + 2e \longrightarrow 2OH^- + H_2 \tag{2}$$

$$\text{Solution:}\quad Cl_2 + H_2O \longrightarrow HClO + Cl^- + H^+ \tag{3}$$

$$HClO \longrightarrow H^+ + ClO^- \tag{4}$$

The loss reactions are:

$$\text{Anode:}\quad 6ClO^- + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 6H^+ + \tfrac{3}{2}O_2 + 6e \tag{5}$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e \tag{6}$$

$$\text{Cathode:}\quad ClO^- + H_2O + 2e \longrightarrow Cl^- + 2OH^- \tag{7}$$

$$\text{Solution:}\quad 2HClO + ClO^- \longrightarrow ClO_3^- + 2Cl^- + 2H^+ \tag{8}$$

$$2ClO^- \longrightarrow O_2 + 2Cl^- \tag{9}$$

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The primary reactions, Reactions 1 and 2, are charge transfer controlled, whereas the loss reactions, Reactions 5 and 7, are usually mass transport controlled [8–9]. At low temperatures ($t < 40^\circ C$) and outside the pH range 4–6, the loss of active chlorine through the chemical formation of chlorate (Reaction 8) is negligible.

In an undivided cell, the current efficiency and the degree of chloride to hypochlorite conversion is thereby limited by the extent of the side reactions, Reaction 5, 6 and 7. The cathodic losses (Reaction 7) are greater than the anodic losses (Reaction 5) since, under diffusion control, as prevails in most cells, the small value of δ_{dl} (diffusion layer thickness) at the cathode (due to evolution of hydrogen gas there) assists in this respect [10].

3. Experimental details

The experimental procedure included a study of the current efficiency, which is dependent on the reduction (Reaction 7), and the oxidation losses (Reactions 5 and 6). The experimental conditions were such that other loss reactions were considered negligible. Two parameters, which influence the current efficiency were controlled, namely the hypochlorite and chlorate concentrations.

The experimental set-up is shown schematically in Fig. 1. The cell was a polypropylene block separated into the anode and the cathode compartments by an anionic membrane (AMV Japan). The distances between the anode, the membrane and the cathode were 10 and 5 cm, respectively. The cathode was a titanium sheet and the anode a titanium sheet coated with RuO_2/TiO_2 by a standard method: the thermal oxidation of thin sprayed-on films of a solution of ruthenium and titanium trichlorides at about 400° C [11]. The dimensions of the electrodes were 4 cm × 4 cm. The electrolyte solutions were prepared by dissolution of reagent grade sodium chloride or sodium hydroxide in distilled water. The anolyte was a NaCl solution of concentrations 0.25, 0.33 and 0.50 mol dm^{-3} (M), and the catholyte was 0.5 mol dm^{-3} (M) NaOH solution. The temperature of the system was kept constant by means of a thermostat ($25 \pm 0.1^\circ C$) in order to suppress the chemical formation of chlorate (Reaction 8).

The concentrations of hypochlorite and chlorate were measured periodically during the course of the experiment. The hypochlorite concentration was determined by potentiometric titration with a solution of 0.05 mol dm^{-3} (M) As_2O_3. After reaching the hypochlorite endpoint, the concentration of the chlorate was potentiometrically titrated with a solution of 0.05 mol dm^{-3} (M) $KBrO_3$ based on the procedure of Ibl and Landolt [8]. The absence of chemical chlorate formation during the experiment was also confirmed by the determination of hypochlorite and chlorate concentrations of the anolyte several hours after the run in the no-current condition.

The 'instantaneous' cathodic and anodic current efficiencies were determined by comparing the volumes of hydrogen and oxygen evolved at the cathode and the anode with that evolved in a standard coulombic cell (with Pt-electrodes and 5% NaOH) connected in series with the experimental cell. These measurements took about 5–10 min, and this was considered to give an 'instantaneous' value.

The overall current efficiency was obtained by monitoring the hypochlorite concentration and the amount of electricity passed during the course of a run.

Most experiments were performed at a constant current density of 100 mA cm^{-2}.

4. Results and discussion

During the electrolysis the rate of hydrogen evolution was constant and did not depend on the hypochlorite

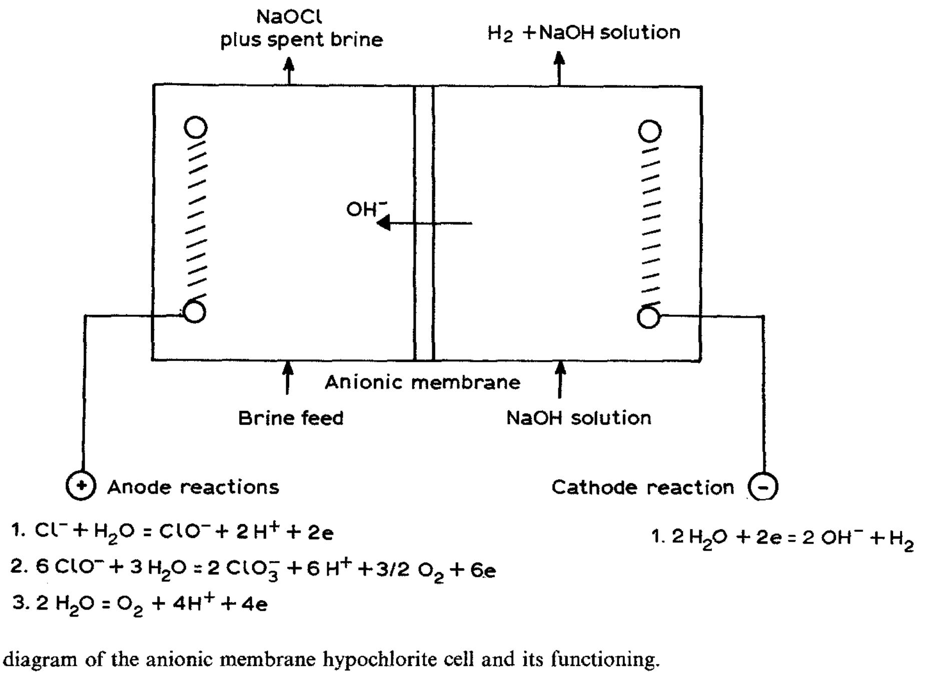

Fig. 1. Schematic diagram of the anionic membrane hypochlorite cell and its functioning.

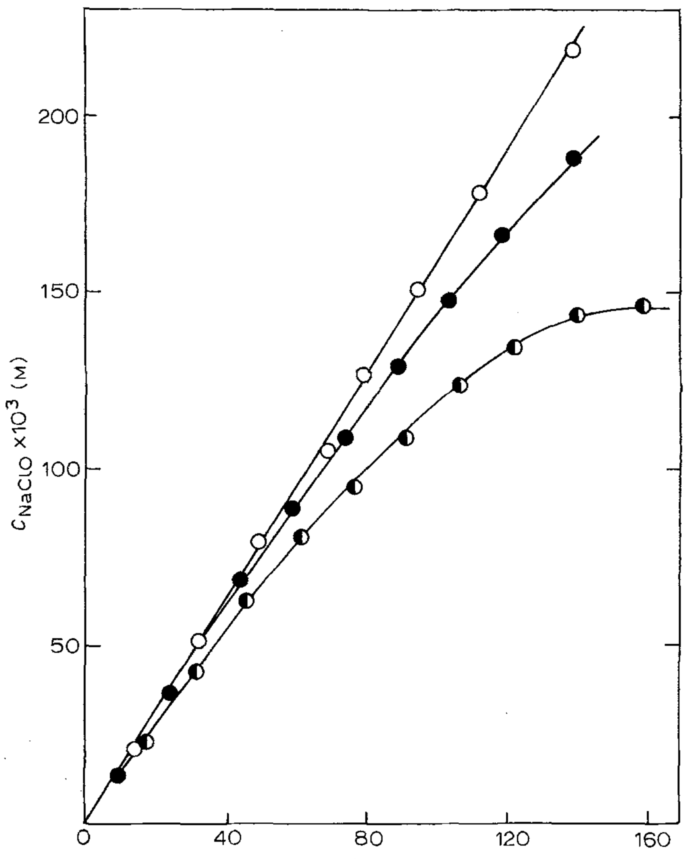

Fig. 2. Concentration of hypochlorite during the batch electrolysis with the following experimental conditions. C_{Cl^-} M: (○) – 0.50, (●) – 0.33, (◐) – 0.25. (t = 25° C, j = 100 mA cm^{-2}, pH 8.3–8.7).

concentration. The pH of the anolyte also remained constant in the range 8.3–8.7. These facts confirm that the back-migrations of ClO^- ions through the membrane did not take place and that OH^- ions were the only charge carriers.

The increase of hypochlorite and chlorate concentrations in the anolyte was followed during the batch electrolysis. The results are shown in Figs 2 and 3. After 2.5 h a steady state hypochlorite concentration was reached only in 0.25 mol dm^{-3} (M) (~ 1.5%) NaCl solution.

Figure 4 shows the dependence of the oxygen evolution rate (given as percentage of the total current applied) on the hypochlorite concentration. At a hypochlorite concentration of about 0.01 mol dm^{-3} (M) there is a rapid drop in the percentage of oxygen evolved. With further increase of the hypochlorite concentration this percentage increases and, eventually, reaches a region of linear dependence. This behaviour indicates that there are two oxygen evolution processes. One is the discharge of water (Reaction 6) and the other is oxidation of hypochlorite (Reaction 5) with the rate being controlled by the mass transport i.e. being linearly dependent on the hypochlorite concentration. By extrapolation to zero concentration one obtains the constant value *a* representing the amount of oxygen evolved by Reaction 6 in the above mentioned region. Conse-

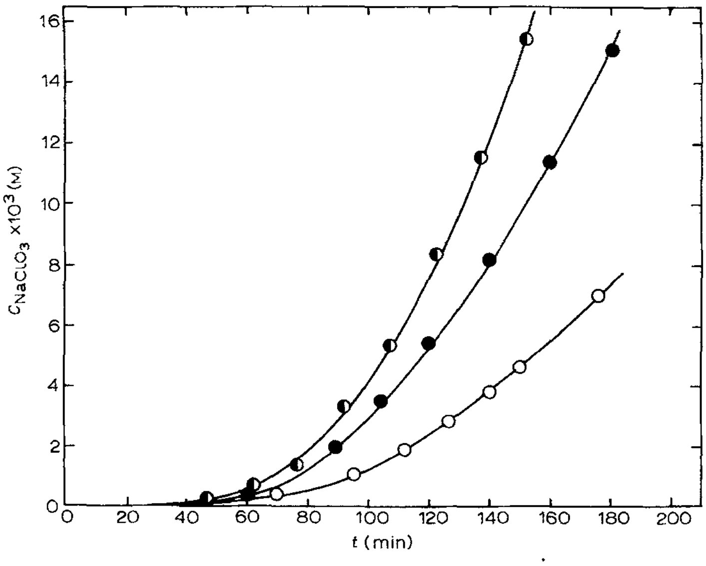

Fig. 3. Concentration of chlorate during the batch electrolysis (experimental conditions are the same as in Fig. 2).

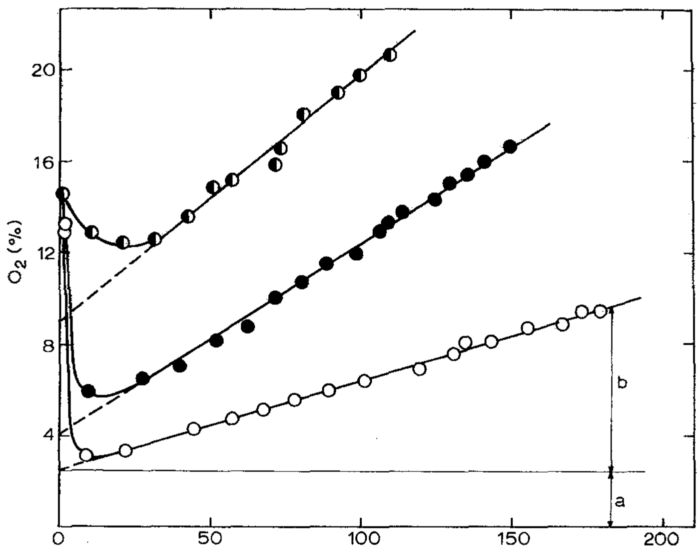

Fig. 4. Oxygen evolved in the examined cell (% of the total current) plotted as a function of hypochlorite concentration at the constant current density. (j = 100 mA cm^{-2}, t = 25°C, pH 8.3–8.7). C_{Cl^-} M: (○) −0.50, (●) −0.33, (◐) −0.25.

quently, b denotes the rest of the oxygen produced by Reaction 5.

The same effect can be seen in Figs 5a–c, showing the change in the overall current efficiency with the hypochlorite concentration for three different chloride contents. This dependence resembles a typical adsorption isotherm which may explain how the presence of chloride and hypochlorite inhibits the reaction of water discharge (Reaction 6). One can assume that the increase in the hypochlorite concentration leads to a blocking of the sites where oxidation of water initially occurred, diminishing the rate of that reaction to a lower constant level a (Figs 5a and b).

Figure 5c shows separated current losses for the two concurrent oxygen evolution reactions: water and hypochlorite oxidation.

To conclude we may say that the anion selective membrane used enabled complete elimination of the

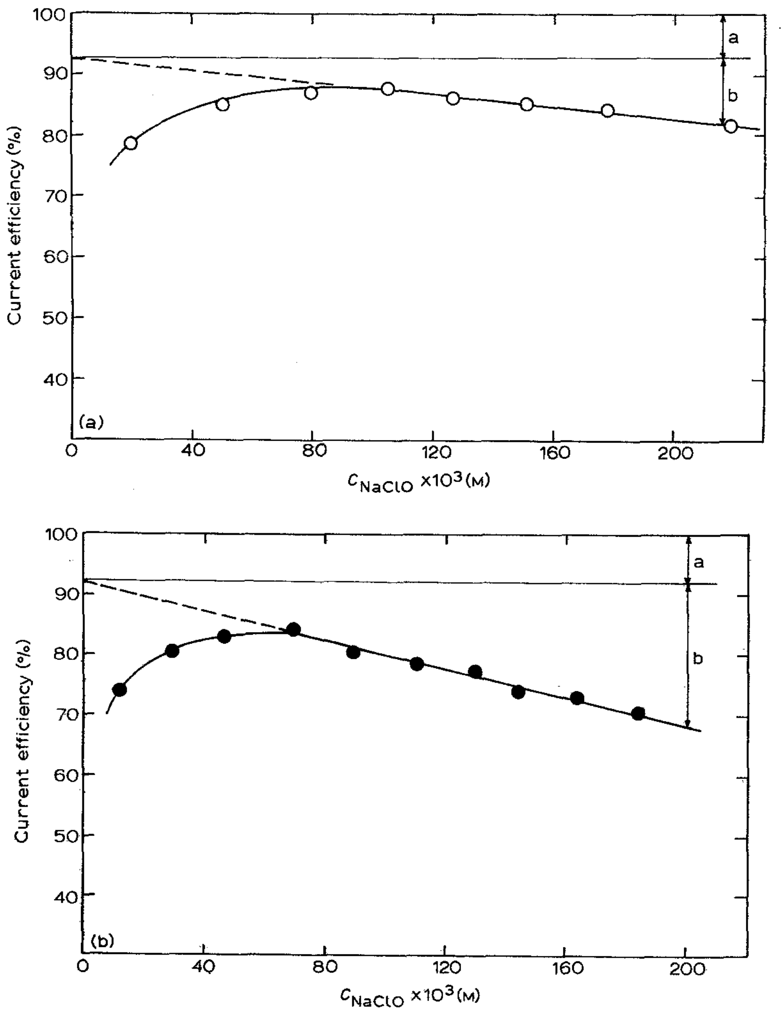

Fig. 5. Overall current efficiency as a function of hypochlorite concentration. C_{Cl^-} M: (a) −0.50; (b) −0.33; (c) −0.25.

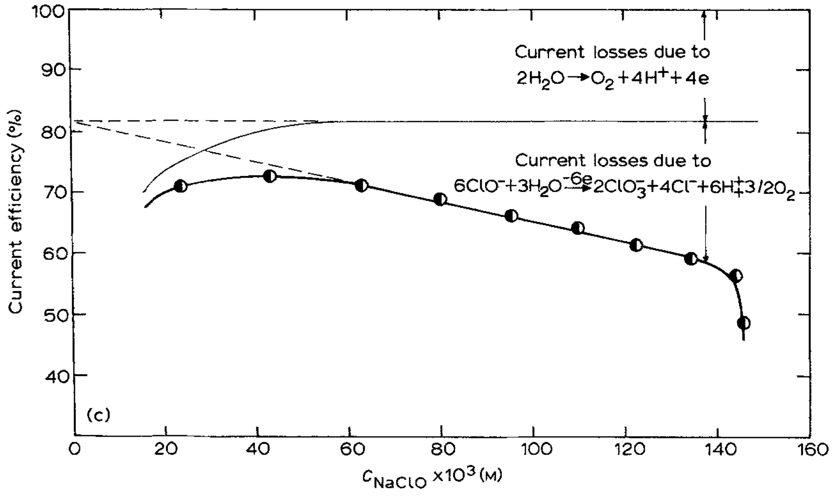

Fig. 5. Continued.

cathodic hypochlorite reduction losses. Relatively high current efficiencies ($\sim$85% for $C_{Cl^-} = 0.5\,mol\,dm^{-3}$ (M)) were obtained and a solution concentration of about 15% NaClO. This is advantageous compared to undivided and chlor-alkali cells with cathionic membrane, keeping in mind that ordinary dilute brine or untreated sea water can be used.

Acknowledgement

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