

Hypochlorite production. I. A model of the cathodic reactions

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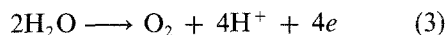
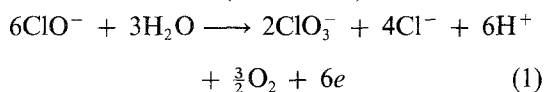
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Based on the results of previous studies, a model for the cathodic reactions in the process of hypochlorite production has been established. The model is described by an equation giving the dependence of the cathodic current efficiency on the hypochlorite concentration and the total cathodic current density. Measurements have shown good agreement with the values predicted by the model, although the diffusion coefficient for hypochlorite ions was not available and a value for the chloride ions was used in the calculations. The cathodic materials used were mild steel, titanium, chromium-plated steel and chromium/molybdenum-plated steel.

1. Introduction

Interest in local electrogeneration of hypochlorite has increased in recent years [1] because of the potential dangers of transporting, storing and handling large volumes of liquid chlorine. Various types of electrolytic cell are in use commercially, the most common being the undivided cell (using either diluted brine or sea water electrolyte), because of its simpler, more economical and easier operation compared with that of divided chlor-alkali cells which incorporate a membrane and use purified brine anolyte [2]. In an undivided cell the electrolyte is pumped between parallel plate electrodes at high velocity to give a large volume of low strength NaOCl, because the maximum attainable hypochlorite concentration is limited by loss reactions.

The loss reactions are mainly concerned with anodic oxidation and cathodic reduction of hypochlorite (Reactions 1 and 2) and anodic oxidation of water (Reaction 3).



At normal operating potentials Reaction 3 is of minor importance. Recently, it was shown [3] that the amount of oxygen evolved increased, due to Reaction 3, when the brine concentration was lowered from 30 to 15 g dm⁻³ NaCl. It was also shown that this reaction can be prevented to a great extent by suitably modified RuO₂-TiO₂ anodes, characterized by a high overpotential for anodic oxidation of water.

Reactions 1 and 2 are usually mass transport-controlled [4, 5]. In the diffusion-controlled regime the cathodic losses are more significant than those at the anode, as hydrogen evolution at the cathode produces a much thinner diffusion layer than that at the anode [6]. Kuhn *et al.* [7] have shown that the cathodic reduction of hypochlorite is inhibited by the precipitation of magnesium and calcium salts from seawater or diluted brine. To a certain extent this reaction can be prevented by a large anode-to-cathode area ratio [8]. It is well known that in industrial chlorate electrolysis the reduction of hypochlorite is suppressed by addition of chromate. It is clear, however, that in the case of hypochlorite production this would not be appropriate because

of the large electrolyte volume. There is some evidence that the same effect can be attained in chromate-free electrolytes by using a chromium-plated cathode [9].

The purpose of this work was firstly to derive a mathematical expression for the theoretical dependence of the cathodic current efficiency on both the hypochlorite concentration and the cathodic current density for the hydrogen evolution reaction; Secondly, to confirm the model using a steel cathode on which the reduction of hypochlorite takes place in the diffusion-controlled regime [5]; and thirdly, to examine the reduction of hypochlorite on chromium and on chromium/molybdenum alloy with oxides included.

2. Experimental details

The electrolyte was prepared from r.g. NaCl and distilled water by adding hypochlorite solution, made from 2 mol dm^{-3} NaOH that had had electrochemically produced chlorine passed through it [6]. Since the hypochlorite concentration was known to be of prime importance for the efficiency losses, special care was taken to study the influence of this variable. The hypochlorite concentration was varied between fairly wide limits ($0\text{--}200 \text{ mmol dm}^{-3}$ NaClO) and kept practically constant during each run. Most of the experiments were carried out at sufficiently high pH (~ 9) and normal temperature (20°C) to suppress chemical formation of chlorate. Before each run the hypochlorite concentration was determined by potentiometric titration with a solution of 0.05 mol dm^{-3} As_2O_3 [6].

The cell was a glass container with an approximate capacity of 1 litre and was kept at the desired temperature by means of a water jacket connected to a thermostat. The cathodic current efficiency (η) was determined by comparing the volume of hydrogen evolved at the cathode with that evolved in a standard coulombic cell (with platinum electrodes and 5% NaOH) connected in series with the experimental cell. Hydrogen was collected in a measuring burette by means of a glass bell hanging over the cathode and submerged to a depth of approximately 5 cm. The cell was operated over the range of cathodic current densities from 10 to 300 mA cm^{-2} .

The cathodic materials were mild steel, titanium, chromium-plated steel and chromium/molybdenum-plated steel. Cathodic samples were rectangular strips, $1 \times 1 \text{ cm}$, suspended in the cell. Both sides of the cathode were made active by placing the cathode between two platinum counter electrodes, 5 cm apart. The chromium cathode was prepared by electrodeposition of chromium onto a steel plate ($1 \times 1 \text{ cm}$) at 40°C and 25 A dm^{-2} from a standard chromium bath (250 g dm^{-3} CrO_3 and 25 g dm^{-3} H_2SO_4). Chromium/molybdenum alloy was deposited on steel using pulsating current from a bath which contained 300 g dm^{-3} CrO_3 and 75 g dm^{-3} $(\text{NH}_4)_2\text{MoO}_4$ [10]. The average current density was 50 A dm^{-2} and the frequency was 187 Hz. The content of molybdenum in the alloy was 3% w/w.

3. Results and discussion

The limiting current for a given diffusion-controlled reaction may be increased by the effect of gas evolution by imposing a current above the limiting current. This is an interactive situation in which an increase in the gas evolution increases the diffusion limiting current of the concurrent reaction.

For a diffusion-controlled reaction, such as the cathodic reduction of hypochlorite, the corresponding limiting current density (mA cm^{-2}) is given by

$$j_h = \frac{n(10^3)FD}{\delta} \quad (4)$$

where d is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) of the hypochlorite ions, C is the hypochlorite ($\text{HClO} + \text{ClO}^-$) concentration (mol cm^{-3}), δ is the thickness of the Nernst diffusion layer (cm), n is the number of exchanged electrons and F is the Faraday constant (A s mol^{-1}).

Janssen and Hoogland [11] and Fouad and Sedahmed [12] have reported data on the thickness of the diffusion layer as a function of the current density of the gas evolved. The general form of the function obtained from the data on hydrogen evolution [11] was

$$\delta = \frac{k}{(j_{\text{H}_2})^m} \quad (5)$$

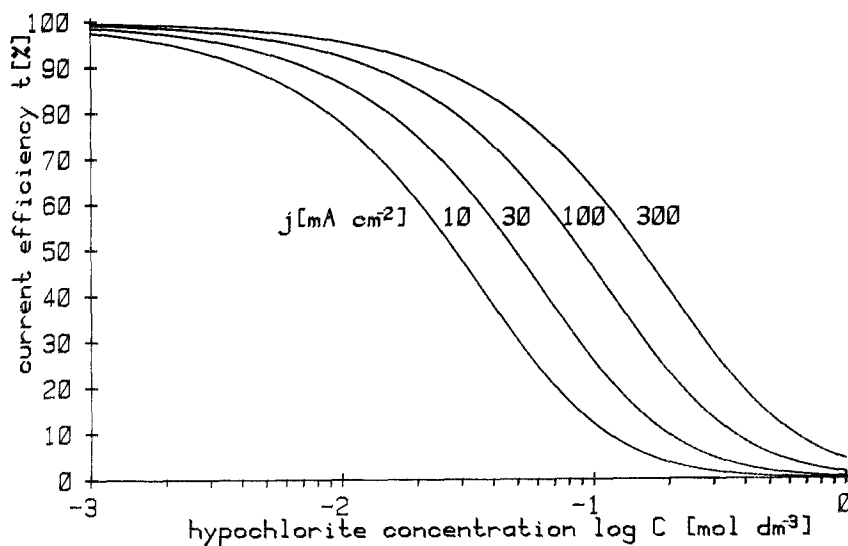


Fig. 1. Theoretically derived plots for current efficiency as a function of hypochlorite concentration at different current densities ($t = 20^\circ\text{C}$; 3% NaCl).

where j_{H_2} is the current density (mA cm^{-2}) of the hydrogen evolution, k is the constant ($= 45 \times 10^{-3}$) for the given height of the electrodes tested ($h = 1\text{ cm}$), and $m = 0.5$.

By introducing the following expressions

$$j_h = j_c - j_{\text{H}_2} \quad (6a)$$

$$t = j_{\text{H}_2}/j_c \quad (6b)$$

where j_c is the total cathodic current density (mA cm^{-2}) and t is the current efficiency for the hydrogen evolution, and by combining Equations 4, 5 and 6 one obtains

$$t^2 - (C^2 K/j_c + 2)t + 1 = 0 \quad (7)$$

where

$$K = \left(\frac{n(10^3)FD}{k} \right)^2 \quad (8)$$

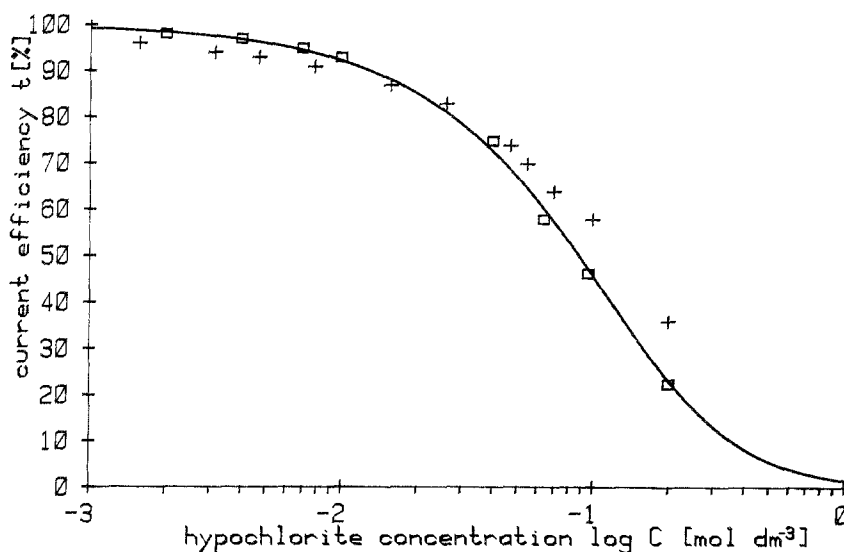


Fig. 2. Comparison between the calculated plot for current efficiency as a function of the hypochlorite concentration (continuous line) and the actual data points obtained on the mild steel (+) and chromium-plated steel cathode (\square); $t = 20^\circ\text{C}$; $j_c = 100\text{ mA cm}^{-2}$; 3% NaCl.

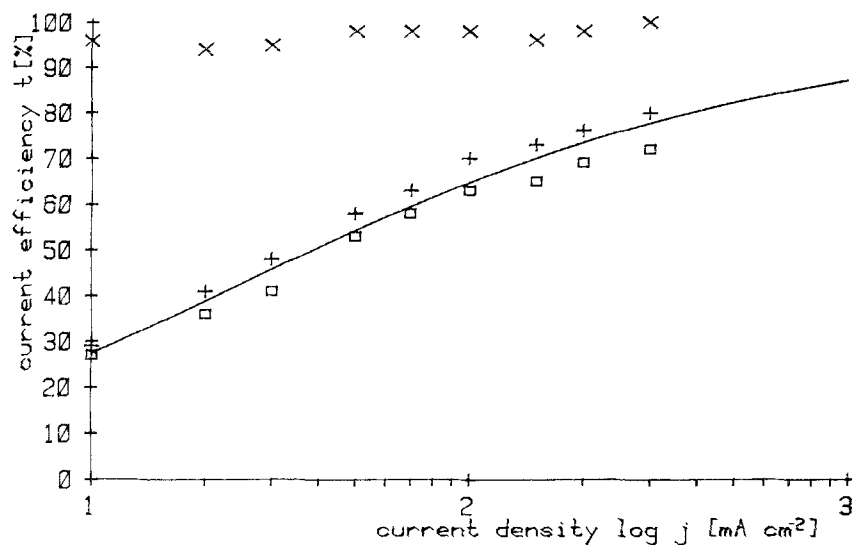


Fig. 3. Cathodic current efficiency as a function of current density. Calculated (continuous line) and actual data points obtained on mild steel (+); chromium-plated steel (□) and chromium/molybdenum-plated steel (×) cathode; $t = 20^{\circ}\text{C}$; 3% NaCl + $5.5 \times 10^{-2} \text{ mol dm}^{-3}$ NaClO solution.

Equation 7 gives the dependence of the cathodic current efficiency (t) on the hypochlorite concentration (C) and j_c .

Being unable to find the value of the diffusion coefficient for hypochlorite ions in the literature, we assumed that this value would not differ

much from that for chloride ions in the same solution. The value $D = 1.86 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for Cl^- ions in 0.5 mol dm^{-3} NaCl was obtained from the plot given by Parsons [13] and was used in our calculation instead of the value for hypochlorite ions. Fig. 1 shows the theoretically

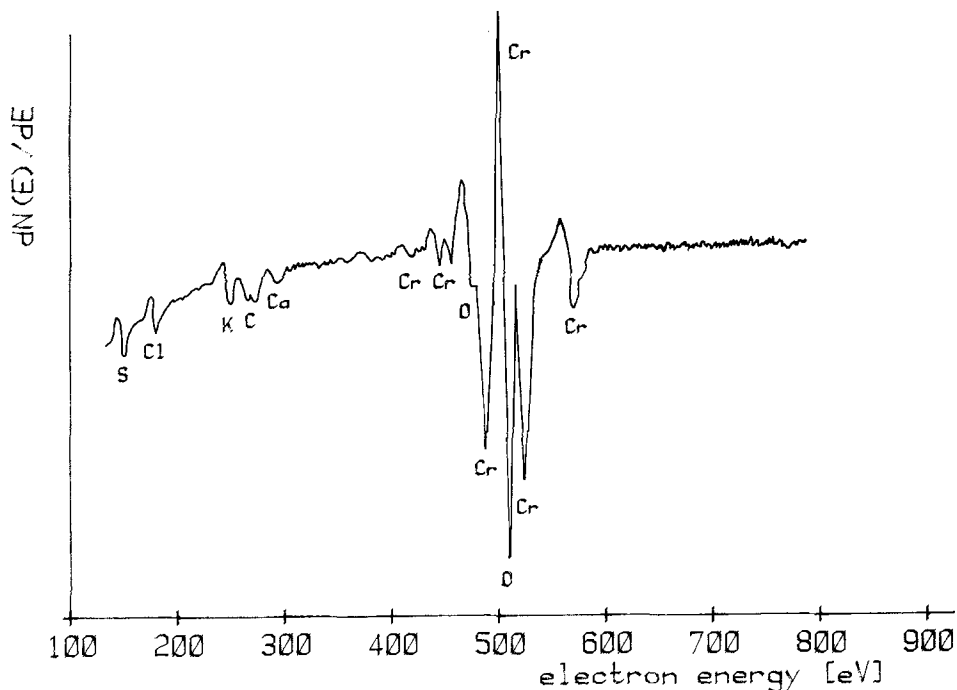


Fig. 4. Auger spectrum of the clean surface of chromium/molybdenum alloy.

derived plots, according to Equation 7, for the cathodic current efficiency against the hypochlorite concentration over the range of cathodic current densities from 10 to 300 mA cm⁻². Figs 2 and 3 show a good agreement between the experimental data points obtained on mild steel (+) and chromium-plated steel (□) cathodes, and the calculated plots for the cathodic current efficiency with the hypochlorite concentration and the cathodic current density, respectively. These results confirm the fact that the reduction of hypochlorite takes place in the diffusion-controlled regime, not only on steel but also on chromium surfaces. Results obtained on the chromium/molybdenum-plated steel (× in Fig. 3) prove that the hypochlorite reduction proceeds at very low rate on the chromium/molybdenum coating and stays almost constant over a wide range of current densities. At first this may seem surprising with respect to the molybdenum content (only about 3%). However, an Auger spectrum (Fig. 4) of a clean chromium/molybdenum surface shows that the major constituent beside chromium is oxygen. The ratio of the Cr/O peaks does not vary with position in the sample, which implies uniform composition of the coating. Also, the fact that ion bombardment has not removed a substantial

amount of the oxygen indicates that its presence in the coating is in the form of an oxide rather than as a contaminant. This is direct evidence that chromium oxide (or hydroxide), and not metallic chromium, largely prevents hypochlorite reduction at the cathode.

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