

REDUCTION OF HYPOCHLORITE AT AN IRON CATHODE IN A CHLORINE ELECTROLYTE

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Reduction of sodium hypochlorite at an iron electrode was studied in order to determine the electrolysis conditions ensuring complete reduction of hypochlorite. The presence of hypochlorite in the electrolytic liquor is undesirable, as it causes corrosion of the equipment and therefore necessitates additional treatment of the liquors. Moreover, in the membrane-diaphragm cell [1] penetration of sodium hypochlorite into the electrolytic liquors leads to oxidation and destruction of cation-exchange membranes.

Reduction of hypochlorite was studied with the aid of polarization curves recorded in electrolytic liquors with various sodium hypochlorite contents and at different brine flow rates.

A graphite anode was used; the cathode was a steel rod of diameter $d = 2$ mm and a surface area of 0.307 or 1.101 cm². A definite potential, measured with a tube voltmeter, was applied to the cathode and the stationary current corresponding to this potential was measured.

The experiments were carried out at 75°C. Typical polarization curves are shown in Fig. 1. It is seen that each curve has a well-defined wave, beginning at a potential in the region of 700 mV with respect to the normal hydrogen electrode, i.e., at a potential below the equilibrium hydrogen potential in the same solution. It is obvious from this that the wave is not related to hydrogen liberation, but, rather, is the wave of hypochlorite-ion reduction. Hydrogen liberation begins under our conditions at a potential of about 1100 mV with respect to the normal hydrogen electrode, which is in good agreement with published data [2]. The proportionality of the limiting current density to the hypochlorite concentration in solution clearly shows that this wave corresponds to reduction of hypochlorite (Fig. 2). Data for cathodes of different sizes do not differ greatly; this indicates that the conditions of convective diffusion are approximately the same in these experiments.

The limiting current of reduction increases fairly appreciably with increase of the velocity of electrolyte flow (Fig. 3). Flow of the electrolyte intensifies supply of hypochlorite to the cathode surface and consequently increases the limiting current of reduction.

The electrolyte flow velocity in an industrial cell can be calculated from the throughout rate, i.e., the current density and alkali concentration. It was found to be $5 \cdot 10^{-4}$ cm/sec under the usual electrolysis conditions. Therefore the flow velocity in an industrial cell is negligible in comparison with the velocities tested, and it can be assumed that the conditions in an industrial cell approximately correspond to our experiments without flow. Both under our experimental conditions and in an industrial cell a certain amount of convective transfer occurs even without flow, quantitative agreement of the data is hardly possible here, but comparison of the orders of magnitude is quite permissible.

According to our data (Fig. 2), the dependence of the limiting current of reduction on the hypochlorite concentration can, on the average, be represented by the following empirical equation:

$$i = 13C, \quad (1)$$

where i is the current density (A/m²) and C is the NaClO concentration (g/liter).

Here the current density is referred to the area of the wire. Usually the current density per unit apparent area of the cathode is of interest. Knowing the diameter of the wires forming the cathode grid and the number of wires per cm² of the overall cathode area, we can calculate their total area. Our calculation.

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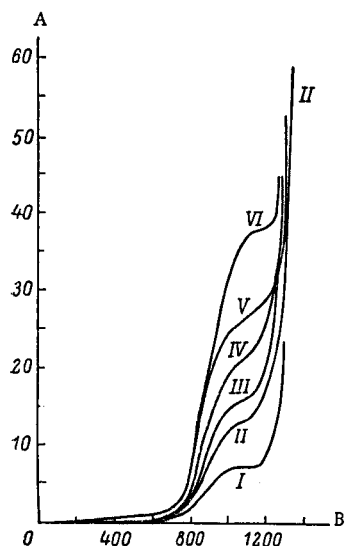


Fig. 1

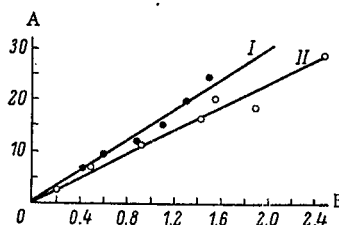


Fig. 2

Fig. 1. Cathodic polarization curves for solutions containing 100 g NaOH and 200 g NaCl per liter and various amounts of NaClO; temperature 75°. A) Current density (A/m^2); B) potential (mV). NaClO contents (g/liter): I) 0.41; II) 0.61; III) 0.88; IV) 1.18; V) 1.30; VI) 1.51.

Fig. 2. Dependence of limiting current on hypochlorite concentration. A) Current density (A/m^2); B) NaClO concentration (g/liter). Cathode area (cm^2): I) 0.307; II) 1.101.

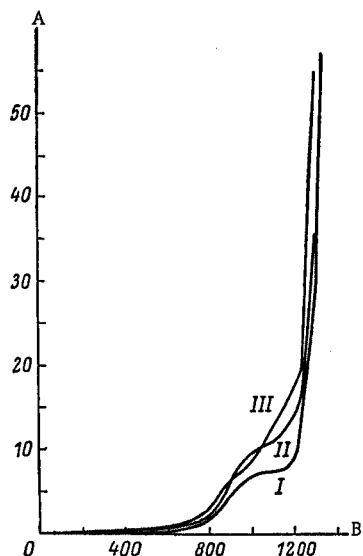


Fig. 3. Cathodic polarization curves at 75° for a solution containing 100 g NaOH, 200 g NaCl, and 0.41 g NaClO per liter at different flow velocities. A) Current density (A/m^2); B) potential (mV). I) No flow; flow velocity (cm/sec): II) 0.55; III) 1.10.

with mutual shielding of the wires at intersections taken into account, gave a value of about two for the ratio of the wire surface area to the overall cathode area.

As we are concerned mainly with the case where hypochlorite is reduced completely and does not pass beyond the cathode, evidently the rear surface of the grid does not come into appreciable contact with solution containing hypochlorite. Therefore only the front part of the surface is involved. Thus, about 1 cm^2 of the true cathode area operates per cm^2 of apparent cathode surface. It may therefore be assumed that the current of hypochlorite reduction per unit cathode area is also represented by Eq. (1) above.

We will now calculate the ratio of the amount of hypochlorite reduced at the cathode to the total hypochlorite content in the liquid flowing past the cathode. The amount of hypochlorite reduced is given by the product

$$q = i \cdot a, \quad (2)$$

where $a = 3.86 \cdot 10^{-4}$ g is the amount of hypochlorite reduced by one coulomb.

Then the amount of hypochlorite reduced per second per cm^2 of cathode area is

$$q = 13 \cdot 10^{-4} \cdot 3.86 \cdot 10^{-4} \cdot C \approx 5 \cdot 10^{-7} \cdot C \text{ g},$$

where 10^{-4} is the factor converting i in A/m^2 to i in A/cm^2 .

The amount of hypochlorite flowing per second through 1 cm^2 is

$$Q = v \cdot C \cdot 10^{-3}, \quad (3)$$

The relation between the throughput rate v and the total current density I , the alkali concentration C_{NaOH} , and current efficiency A is given by the expression

$$v = \frac{A \cdot I}{100 \cdot C_{\text{NaOH}} \cdot F}, \quad (4)$$

where F is the cathode area.

The fraction of hypochlorite reduced is given by the ratio q/Q . Substituting numerical values of the constants into Eqs. (1)–(4), we have

$$\frac{q}{Q} = \frac{0.05}{I} \cdot C_{\text{NaOH}},$$

where C_{NaOH} is the alkali concentration (g-eq/liter).

The current efficiency is assumed to be 96%. It follows from this formula that the ratio $q/Q = 1$, i.e., complete reduction of all the hypochlorite formed at 500 A/m² current density is reached at 1 M NaOH concentration (40 g/liter), and at 1000 A/m² current density at 2 M NaOH concentration (80 g/liter). At lower alkali concentrations at these current densities hypochlorite must penetrate into the catholyte.

Indeed, in practical operation in this range of current densities breakthrough of hypochlorite into the catholyte usually ceases at alkali concentrations of the order of 50–100 g/liter, and hypochlorite is always present in the catholyte at low concentrations. Of course, this is not an exact calculation, because our experimental conditions are not fully comparable to those in an industrial cell. However, the orders of magnitude are quite reasonable.

These results were also used for assessment of the behavior of sodium hypochlorite in a membrane-diaphragm cell. In this cell an ion-exchange membrane is placed between the cathode and the anode, while between the membrane and the anode there is a permeable diaphragm deposited on an auxiliary cathode. The current density at the auxiliary cathode must be as low as possible, but high enough to prevent penetration of hypochlorite to the membrane.

A calculation of the type given above showed that under the operating conditions of the membrane-diaphragm cell the limiting current density of hypochlorite reduction is about 30 A/m². As it is necessary to allow a certain margin in case of deviations from normal operation, a current density of 50 A/m² was adopted for the auxiliary cathode. At this current density there was never any breakthrough of hypochlorite beyond the auxiliary cathode during prolonged operation (about 2 months) of the membrane-diaphragm cell.

LITERATURE CITED

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2. G. N. Kokhanov and E. M. Kuchinskii, Zh. Fiz. Khim., **36**, No. 3, 480 (1962).