

of the ionic structure of nitrite melts and confirms the absence of correspondence between the liquidus curves in the phase diagrams and the form of the property isotherms (Fig. 9).

Analogous facts came to light in the system of sodium, potassium, and calcium nitrates, the components of which form the compound $4\text{KNO}_3 \cdot \text{Ca}(\text{NO}_3)_2$.⁶ The constant-density lines, regardless of the crystallisation fields which they intersect, are almost linear and parallel to the sodium nitrate-potassium nitrate side of the triangle.

However, Luzhnaya and Vereshchetina found that in a number of systems with heteroionic compounds of the type of kainite, the formation of the compounds is reflected in the density and molar-volume isotherms⁷⁻⁹. This appears to indicate that nitrite and nitrate melts have a simpler structure than those of halides, sulphates, etc. This is also evidenced by conductivity data. The above difference in the molecular state of salts in melts is most probably due to different types of chemical bonds being present.

SUMMARY

1. The densities of melts in the ternary system of sodium, potassium, and barium nitrites have been measured; density isotherms of internal sections and the component binary systems are linear.
2. The molar-volume isotherms of the binary systems and internal sections of the ternary system are additive.
3. The formation of the compound $\text{KNO}_3 \cdot 2\text{Ba}(\text{NO}_3)_2$ is not reflected in the density and molar-volume isotherms, which means that it is completely dissociated in the melt.
4. There is no correspondence between the type of liquidus curves in the phase diagrams and the density and molar-volume isotherms.

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HYDROGEN OVERVOLTAGE OF OXIDISED IRON CATHODES IN AN ALKALINE CHLORIDE SOLUTION

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Practical suggestions for the reduction of the cathode potential in a cell for the electrolysis of chlorides have been made on the basis of studies of hydrogen overvoltage in aqueous alkali¹⁻³ and alkaline chloride solutions⁴⁻⁸. However, experimental tests of some of the recommendations did not give the expected results. The necessity therefore arose for a more detailed study.

Previous investigations⁴⁻⁸ were made in conditions such that the entry of anodic products (hypochlorite and chlorate) to the cathodic compartment was prevented. Since in the cell used for the electrolysis of chloride there is a stream of liquid from the anodic to the cathodic compartment, we also investigated the effect of the anodically produced hypochlorite on the cathodic process.

EXPERIMENTAL

The experiments were carried out in a usual electrolytic cell⁹, made of Jena glass and provided with reflux condensers to avoid loss of water vapour. The cathodic and anodic compartments were separated by a sintered glass diaphragm and an immersion-type tap. The hydrogen electrode was a palladised palladium plate. To prevent the access of anodically produced hypochlorite to the cathode compartment, the anode compartment, the connecting tube on either side of the glass diaphragm, and the tap were filled with 3 N NaOH without chloride. The cathodic and hydrogen electrode compartments were filled with a solution containing 120 g litre⁻¹ NaOH + 190 g × litre⁻¹ NaCl. Sodium hypochlorite was added periodically in an amount such that its concentration in the cathodic compartment was ~0.5 g litre⁻¹. During an experiment purified hydrogen was bubbled through the solution in the cathodic compartment. The temperature of the cell was maintained constant within ±0.2°. The overvoltage was measured with a P-4 potentiometer.

The test solutions were prepared by diluting with twice-distilled water a concentrated solution of alkali. The latter was prepared by dissolving NaOH ("chemically pure"), washed free of carbonate, in twice-distilled water and then purifying it by electrolysis for two days in a cell with platinum electrodes. NaCl ("chemically pure" grade) was recrystallised from twice-distilled water and ignited for 1 h at 400° before dissolution. In repeated experiments "chemically pure" NaCl was used without purification, and this had no appreciable effect on the reproducibility of the results.

The cathodes were prepared from spectroscopically pure iron. The air-oxidised cathodes were made by allowing a natural oxide film to form, during prolonged exposure to air, on an initially bright and smooth iron surface. To prepare the thermally oxidised electrodes, air-oxidised electrodes were heated in air at 475° ± 5° for 15 min.

In experiments on the transfer of potential to the diffusion side "Armco" iron 0.1 mm thick was employed. The cathode was made in the form of a disc, thoroughly

polished, washed with alcohol, and fixed with BF-2 adhesive between the two flat end-pieces (diameter of each piece was less than that of the cathode) of the polarisation and diffusion parts of the apparatus. The adhesive was polymerised at 60° – 70° for 3–4 h.

Special experiments on the reduction of the oxide layers were not undertaken. The potentials were determined by means of a cathodic voltmeter. An air thermostat accurate to $\pm 2^{\circ}$ was employed.

Cathodic voltmeters were used in the visual determination of the curves showing the full potential after the current had been switched off.

DISCUSSION

Figs. 1 and 2 show that there is a considerable decrease in the overvoltage with time at the beginning of polarisation at 25° with both air and thermally oxidised cathodes in a solution without hypochlorite when $D_c = 4 \text{ mA cm}^{-2}$. There is also some drop in the overvoltage with time at the remaining current densities except for $D_c = 200 \text{ mA cm}^{-2}$ ($\eta > 0.5 \text{ V}$), which, in the case of an air-oxidised cathode, results in a slight rise of the overvoltage after an initial fall. The decrease in the overvoltage with time, which is particularly marked at the beginning of polarisation when

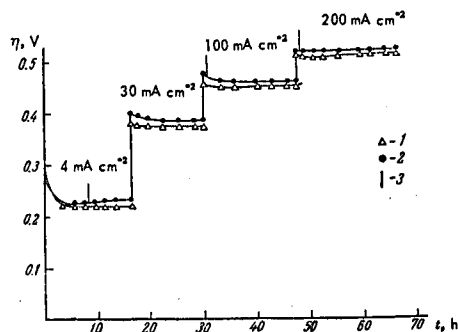


Fig. 1. Variation of the overvoltage of the air-oxidised cathodes at 25° with the current density and polarisation time:

1) solution without hypochlorite; 2) solution with hypochlorite; 3) moment of introduction of hypochlorite.

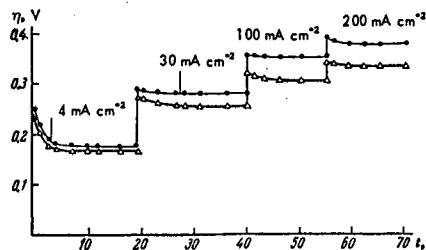


Fig. 2. Variation of the overvoltage of the thermally oxidised cathodes at 25° with the current density and polarisation time. For key see Fig. 1.

$D_c = 4 \text{ mA cm}^{-2}$, may be explained, on the basis of published data^{10,11}, by the reduction of iron oxides and an increase in the surface area, which is more pronounced with thermally oxidised electrodes.

At the beginning of polarisation ($D_c = 4 \text{ mA cm}^{-2}$) at 50° the overvoltage for both air (Fig. 3) and thermally (Fig. 4) oxidised cathodes falls slightly at first and then begins to increase. At current densities of 100 and 200 mA cm^{-2} the overvoltage of the air-oxidised cathode only increases with time, the increase being greatest at $D_c = 200 \text{ mA cm}^{-2}$.

At 80° and $D_c = 4 \text{ mA cm}^{-2}$ the overvoltage of both the air (Fig. 5) and thermally (Fig. 6) oxidised electrodes sharply increases with time. At the remaining current densities the overvoltage also rises, but to a lesser extent in the case of the thermally oxidised electrode.

A decrease in the overvoltage of the air-oxidised cathode (Fig. 5), which occurs at 30 mA cm^{-2} and can also be seen in some cases at $D_c = 4 \text{ mA cm}^{-2}$, is unrelated to the process examined here and will be discussed in another communication.

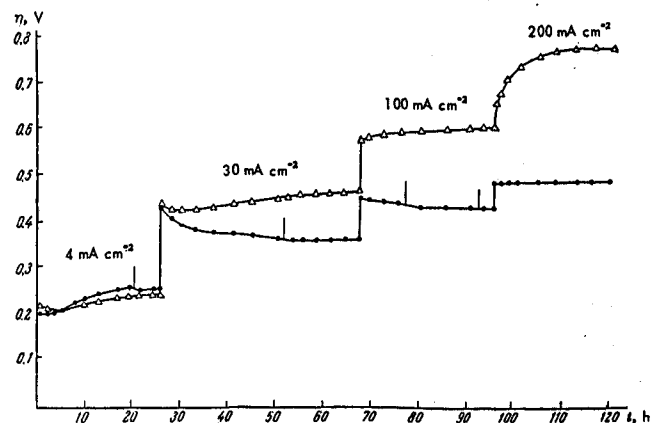


Fig. 3. Variation of the overvoltage of the air-oxidised cathodes at 50° with the current density and polarisation time. For key see Fig. 1.

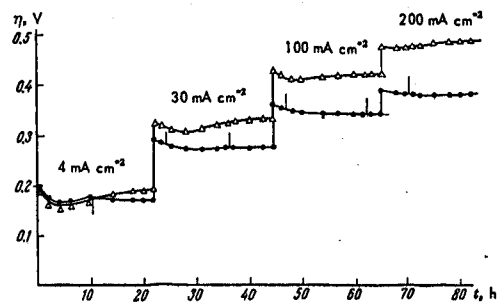


Fig. 4. Variation of the overvoltage of the thermally oxidised cathodes at 50° with the current density and polarisation time. For key see Fig. 1.

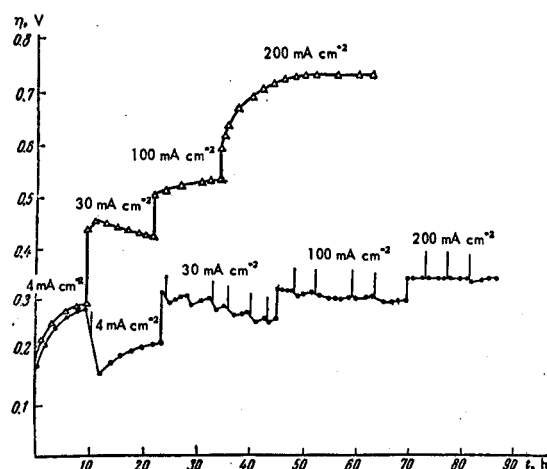


Fig. 5. Variation of the overvoltage of the air-oxidised cathodes at 80° with the current density and polarisation time. For key see Fig. 1.

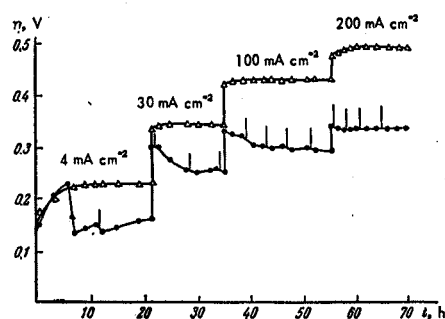


Fig. 6. Variation of the overvoltage of the thermally oxidised cathodes at 80° with the current density and polarisation time. For key see Fig. 1.

Figs. 1–6 show that at $D_c = 4 \text{ mA cm}^{-2}$ in a solution without hypochlorite the lowest initial overvoltage of both the air and thermally oxidised cathodes occurs at 80°, the highest at 25°, with an intermediate value at 50°. Comparison of the steady-state overvoltages shows that in the case of the thermally oxidised cathodes this is true at all current densities. The steady-state overvoltages of the air oxidised cathodes are also higher at 80° and 50° than at 25°. Thus the overvoltage of an iron cathode in a solution without hypochlorite exhibits an unusual temperature variation, increasing with increase in the temperature. This behaviour is a consequence of the rise in overvoltage with time, which becomes more rapid at higher temperatures. Experiments in a solution containing hypochlorite are essential for an explanation of the reasons underlying the rise in overvoltage.

Since hypochlorite has a very high oxidation potential¹², it is possible that it can oxidise the surface of the cathodically polarised iron. This is apparently the

explanation of the rise in the overvoltage (Figs. 1 and 2) at 25° in a solution containing hypochlorite. The higher overvoltage in the hypochlorite solution at 4 mA cm^{-2} is evidence, even at this current density, that hypochlorite behaves more as an oxidising agent than as a depolariser.

Introduction of hypochlorite at 50° (Figs. 3 and 4) and 80° (Figs. 5 and 6) leads to a considerable decrease in the overvoltage compared with the value observed in a solution without hypochlorite. At $D_c = 200 \text{ mA cm}^{-2}$ the fall in the overvoltage of the air-oxidised cathodes reaches $\sim 0.3 \text{ V}$ and of the thermally oxidised cathode $\sim 0.1 \text{ V}$. The corresponding values for 80° are ~ 0.39 and $\sim 0.16 \text{ V}$.

The fall in the overvoltage in the presence of hypochlorite at 50° and 80° is evidence that its action is not the same as at 25°. Further, the extent of the decrease after addition of hypochlorite at intermediate (30 mA cm^{-2}) and high (100–200 mA cm^{-2}) current densities (Figs. 3–6) shows that the direct effect of the discharge of hypochlorite on the overvoltage is slight.

A considerable accumulation of hypochlorite on the cathode surface is improbable because, as mentioned above, the hypochlorite ion has a very high oxidation potential and is easily reduced. Consequently, the effect of hypochlorite on the cathode, resulting in a fall of the overvoltage, may be to prevent the accumulation of hydrogen on the surface and in the bulk of the cathode or, if the accumulation has already taken place, to facilitate the removal of the adsorbed hydrogen.

The correctness of this conclusion is confirmed by the determination of the fall in potential after the current has been switched off (Fig. 7). The experiment was carried out as follows. Thermally oxidised electrodes were polarised at 80° and $D_c = 200 \text{ mA cm}^{-2}$ for 70 h. One of the electrodes was placed in a solution without hypochlorite and another in a solution into which hypochlorite was periodically introduced. The temperature was then reduced to 25° and the polarisation continued for a further 8 h, without adding more hypochlorite. The overvoltage in the solution without hypochlorite became stabilised at 0.684 V and in the hypochlorite solution at 0.481 V. After that the current was switched off, and the fall in potential was observed visually.

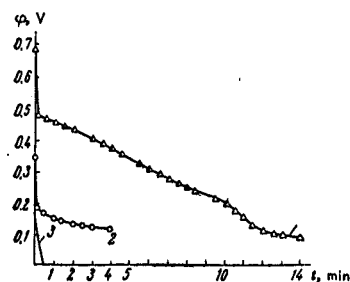


Fig. 7. Curves showing the fall in potential after the current has been switched off: 1) in a solution without hypochlorite; 2) in a solution with hypochlorite; 3) calculated by Eqn. (1).

The curve shows that the electrode polarised in a solution without hypochlorite (Fig.7, curve 1) retains a high cathodic potential for a long time, with vigorous evolution of hydrogen for ~ 10 min. Since under our conditions the formation of a sodium-iron alloy is unlikely, the long duration of the fall in potential must be due to a large amount of hydrogen absorbed by the cathode.

Comparison of curves 2 and 3 (Fig.7) shows that the cathode does not absorb much hydrogen in a solution with hypochlorite. Curve 3 was obtained from the equation for the fall in potential due to discharge of the double layer:

$$\eta_t = \eta_0 - b \log \left(1 + \frac{2.3i_{\text{ad}}}{C_V} \right), \quad (1)$$

the derivation of which¹³ presumes the existence of a semilogarithmic relation between the rate of evolution of hydrogen and the electrode potential, and does not take into account the hydrogen dissolved in the bulk of the electrode. The calculation was based on the value of V ($V = 0.12$) and the maximum capacitance ($3000 \mu\text{F cm}^{-2}$) determined experimentally for a thermally oxidised electrode (in the range covered by the fall in potential) using alternating current at 2000 c/s.

The correctness of the above conclusion is confirmed by the following observations.

1. In experiments on the transfer of potential to the diffusion side at 80° addition of hypochlorite on the polarisation side at $\eta \leq 0.3$ V caused a positive shift in the potential on the diffusion side. Consequently, hypochlorite reacts with the hydrogen adsorbed on the metal surface, facilitating a reduction in the concentration of hydrogen in the bulk of the cathode.
2. The strength of a tantalum electrode was not appreciably reduced after polarisation for 24 h at 80° and a current density of 30 mA cm^{-2} in a solution containing hypochlorite. A similar cathode (tantalum wire 1.4 mm in diameter and 13 mm long) polarised in the same way but in a chloride solution without hypochlorite broke on shaking. The loss in strength in the latter case is due to absorption of hydrogen.
3. We have frequently observed visible blistering of the cathode surface following prolonged polarisation at 80° in a solution without hypochlorite. The same observation was made by one of us during electrolysis in an alkaline solution¹¹. Similar polarisation in a solution containing hypochlorite does not produce blisters.

The above results show that hypochlorite prevents the accumulation of hydrogen on the surface and in the bulk of the cathode. We have established that the effect of hypochlorite on an iron cathode, resulting in a fall of the overvoltage, consists in the removal of hydrogen on the surface or in the bulk of the metal. Consequently, the experimental data also demonstrate that the increase in the overvoltage with time is due to the absorption of hydrogen by the cathode. One of us has noted¹¹ that the increase in the overvoltage at 25° of an iron cathode in an alkaline solution above 0.5 V is due to the complete removal of oxide layers from the electrode surface and the accumulation of hydrogen on the surface and in the bulk of the cathode. The behaviour of an iron cathode at 50° and 80° substantially differs from that at room temperature. At the higher temperatures the increase in the overvoltage with time occurs at $\eta < 0.5$ V (Figs.5 and 6). If it is supposed that the rise in the overvoltage at $\eta < 0.5$ V occurs because higher temperatures facilitate the removal

of oxygen from the cathode surface and its replacement by hydrogen, a shift of the characteristic point at $\eta \sim 0.5$ V towards more positive potentials, and its disappearance at $\eta > 0.5$ V, would be expected. However, the experimental data show that the position of this point does not change much, a secondary rise in the overvoltage occurring here.

Our experiments on the transfer of potential to the diffusion side have shown that at 25° , 50° , and 80° adsorption and absorption of hydrogen take place at $\eta \leq 0.2$ V, i.e. potentials at which, according to ref.11, the oxide layers have not been removed from the cathode surface. Consequently, reduction of the oxides and adsorption and absorption of hydrogen occur at the same time and over a wide range of overvoltages. The most complete explanation of our experimental data may be obtained on the assumption that the increase in the overvoltage at $\eta < 0.5$ V is due to a change in the adsorption properties of the cathode surface for hydrogen. This change occurs because polarisation of the cathode and penetration of hydrogen into the metal result in the formation (up to saturation), at the given η , of Fe-H bonds on the inner side of the surface layer of iron atoms. While this process occurs on the inner side of the surface layer, the bonding energy of adsorbed hydrogen on the outer side diminishes, which results in an increase of the overvoltage. For the above process to take place, complete removal of the oxide layers from the cathode surface is not essential, because hydrogen is absorbed even when the oxides are still present ($\eta \leq 0.2$ V).

The experimental data show that the formation (up to saturation) of Fe-H bonds takes place slowly, being facilitated by higher temperatures, and depends on the potential. At higher temperatures the increase in the overvoltage due to absorption of hydrogen by the cathode and the change in the adsorption properties of the latter for hydrogen are so pronounced that the steady-state overvoltage becomes greater than at 25° .

In a solution containing hypochlorite the above processes take place to a much smaller extent, so that the usual temperature variation of the overvoltage is observed. At industrial current densities and 80° the overvoltage of the air and thermally oxidised electrodes is close to 0.25 V.

The experimentally observed (Figs.1 and 2) decrease in the overvoltage and the effect of hypochlorite are evidence that at 25° and $\eta < 0.5$ V processes connected with the reduction of oxide layers exert a dominant effect on the time variation of the overvoltage.

When the temperature is raised to 50° and 80° the change in the overvoltage with time depends more on processes involving adsorption and absorption of hydrogen than on the removal or formation of surface oxides. Since the overvoltages obtained during rapid measurements with decreasing current density (Fig.8) are higher, it follows that the rise in the overvoltage with time at $\eta > 0.5$ V is due to a substantial secondary change in the surface properties of the cathode.

Balmakov and Zamotorin¹⁴ have established that under certain conditions dissolved hydrogen can react with iron to form new phases. Kuchinskii and Veselovskaya¹¹ have shown that a hydride of iron may be formed at an overvoltage greater than 0.5 V. Thus the observed considerable rise in the overvoltage, at $\eta > 0.5$ V, of the air oxidised cathodes at 50° and 80° and a smaller rise at 25° (Fig.1) may be attributed to the formation of a hydride with the properties of a new phase. The presence of a plateau

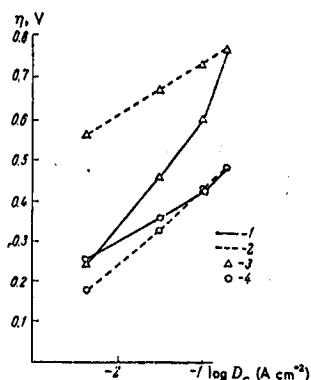


Fig. 8. Variation of the overvoltage with $\log D_c$ for the air-oxidized cathodes at 50°:

- 1) steady-state overvoltages; 2) rapid measurements in the reverse order;
- 3) solution without hypochlorite;
- 4) solution with hypochlorite.

at $\eta \sim 0.48$ V on the curve for the fall in potential may show the existence of such a hydride¹¹.

The suggested formation (up to saturation) of Fe-H bonds is more consistent with our and literature data than explanations which interpret the rise in the overvoltage merely in terms of quantitative changes in the hydrogen concentration on the surface and in the bulk of the electrode.

The experimental data obtained by Past¹⁵ confirm the above suggestions. Past showed that, as the overvoltage increases, the capacitance of an iron electrode, calculated from the initial section of the potential-fall curve, decreases. After the potential has continued to fall for a time, however, the capacitance increases markedly. The higher the initial potential, the lower the initial capacitance and the higher its increase following a prolonged fall in potential.

On the basis of the above explanation the decrease in capacitance and hence in the quantity of the electrochemically active hydrogen, *i.e.* hydrogen capable of undergoing exchange with solution, observed when the overvoltage increases, may be attributed to a diminution of the bonding energy of this hydrogen with the cathode surface. The diminution is a consequence of the formation of Fe-H bonds discussed above. The increase in the capacitance as the potential continues to fall may be explained by the rupture of the Fe-H bonds with decrease in potential, which results in the activation of the hitherto electrochemically inactive, bound hydrogen, and hence in a slowing down of the potential fall and in an increase of the capacitance. Since increase in potential leads to a greater total amount of hydrogen in the surface layer of the cathode, the rise in capacitance with time is greater, the higher the initial potential.

SUMMARY

1. A study has been made of the hydrogen overvoltage of air and thermally oxidized iron cathodes at 25°, 50°, and 80° in solutions containing 120 g litre⁻¹ NaOH + 190 g litre⁻¹ NaCl with and without added hypochlorite.
2. The increase in the overvoltage with time, both of the air and thermally oxidized cathodes, observed at 50° and 80°, is due to absorption of hydrogen by the cathode.
3. The presence of hypochlorite increases the increase in the overvoltage at higher temperatures.
4. At higher temperatures hypochlorite prevents the accumulation of hydrogen on the surface and in the bulk of the cathode.
5. In a solution containing hypochlorite at 80° and at current densities employed nowadays in industry the hydrogen overvoltage of the oxidized cathodes is ~ 0.25 V.
6. An explanation put forward for the rise in the overvoltage with time at 50° and 80° postulates that the rise is due to a diminution in the bonding energy of the adsorbed hydrogen with the surface layer of atoms on the cathode. It is suggested that the diminution is due to the formation (up to saturation) of Fe-H bonds on the inner side of the surface atomic layer (at $\eta < 0.5$ V), or to the formation of a fairly stable hydride of iron (at $\eta > 0.5$ V), possessing the properties of a new phase.

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