

INVESTIGATION OF THE EFFECT OF ELECTROLYSIS CONDITIONS ON THE STABILITY OF GRAPHITE ANODES IN THE CHLORINE CELL*

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Translated from *Zhurnal Prikladnoi Khimii*, Vol. 34, No. 7,

pp. 1537-1542, July, 1961

Original article submitted April 19, 1960

The problem of the wear of graphite anodes, important in the production of electrolytic chlorine, has been studied repeatedly [1-9], but many of its aspects must be regarded as still unsolved. In particular, the influence of anolyte acidity has been studied very little; yet this factor may be of great significance, because the cause of destruction of the graphite is oxidation by the oxygen liberated at the anode.

The method widely used for accelerated testing of anode stability [1-6], in which the anodic liberation of oxygen is greatly accelerated by suitable choice of the electrolyte composition, cannot be used for quantitative characterization of the relationships in industrial electrolysis.

Determinations of anode wear in laboratory models of diaphragm cells [7, 8] have been carried out either without account being taken of the specific features of diaphragm cell operation [10], so that in some experiments there was extensive penetration of alkali into the anolyte with a consequent sharp increase of wear, or under conditions very different from those applying industrially; in particular, at low temperatures [8].**

The anode process on graphite was studied under more specific conditions by Filippov et al. [9], who used a rapidly flowing electrolyte and determined the ratio of the amounts of chlorine and oxygen (free and combined) liberated from the composition of the gas formed during electrolysis. However, mechanical wear of the anode (crumbling of graphite particles) is not taken into account in this method. These experiments were relatively short, so that a steady state of the electrode surface could not be guaranteed, and because of the high flow rate of the anolyte its acidity was very low in most of the experiments.

We used a method for determining anode wear under the normal electrolysis conditions in a diaphragm chlorine cell, and steps were taken to prevent or greatly reduce penetration of alkali into the anode compartment.

EXPERIMENTAL

The laboratory cell is shown in Fig. 1. The use of a completely filled cathode compartment with a corresponding reserve of anolyte level favors uniform and controllable operation of the asbestos diaphragm [10]. The large distance between the electrodes and the presence of a second diaphragm made of glass fabric prevent convective transfer of alkali penetrating from the catholyte directly to the anode; this alkali is neutralized in the space between the diaphragms. This was confirmed by the observed fact that the anolyte acidity was consistently higher than the acidity of the liquid in the space between the diaphragms.

The anodes were inserted through slots in the cell lid. The diaphragm was formed with the use of spare anodes, and the electrodes to be tested were introduced into the cell after the catholyte and anolyte compositions had reached a steady state.

Some of the experiments were performed with cells of similar design but with a smaller distance between the electrodes and without a glass fabric diaphragm.

* Communication I.

** In the investigation [8] only five determinations of anode wear were carried out, under very different conditions in each case.

Graphitized anodes from the Dnepr electrode factory were used for the experiments. The specimens (average dimensions $100 \times 90 \times 9$ mm) were cut from electrode blocks so that the working surface corresponded to a section of a block at a distance of 15-20 mm from its external surface. This eliminated the influence of the more compact external layer.

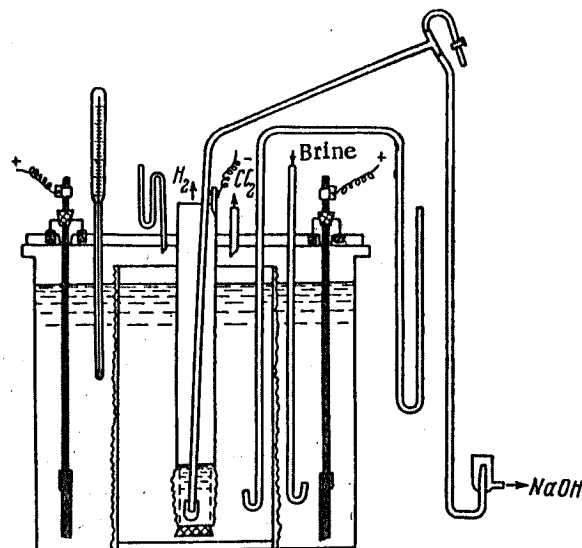
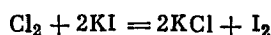


Fig. 1. Laboratory cell.

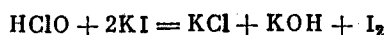
The anodes were tested continuously for 15-30 days. During this time 5000-10,000 amp-hr was passed through the cell. The quantity of electricity was recorded by means of a mercury meter. The current density was 800 amp/m^2 and the temperature was 80° .

The brine used for electrolysis contained 300 g NaCl per liter; it was freed from alkaline-earth and heavy metals, sulfates, and carbonates, and was made suitably acid or alkaline.

The catholyte and anolyte were analyzed daily. The contents of NaOH, NaClO, NaClO₃, NaCl, Na₂SO₄ were determined. The anolyte acidity was determined by titration with 0.1 N NaOH, after iodometric determination of active chlorine in the same sample. Here the reaction



is accompanied by a reaction with the HClO formed by hydrolysis of chlorine:



Because of the latter reaction, the acidity determined by analysis $[\text{H}^+]$ is less than the true acidity (H^+) by the value of the HClO concentration:

$$[\text{H}^+] = [\text{H}^+] - (\text{HClO}).$$

We disregard the ClO⁻ ion content, because even in weakly acidic solutions its concentration is several orders of magnitude lower than that of HClO.

Substituting the expression for (HClO)

$$(\text{HClO}) = \frac{K_h}{(\text{H}^+)(\text{Cl}^-)\gamma_{\text{H}^+}\gamma_{\text{Cl}^-}} (\text{Cl}_2) = \frac{K_h}{(\text{H}^+)(\text{Cl}^-)\gamma_{\text{H}^+}\gamma_{\text{Cl}^-} + K_h} [\text{Cl}_2],$$

For selection of anodes of approximately the same degree of graphitization their resistivity was measured, as this is an approximate measure of the degree of graphitization. Anodes of resistivity greater than $10 \text{ ohms} \cdot \text{mm}^2/\text{m}$ were used. This value was chosen on the basis of a special investigation carried out by Z. I. Lifatova, L. M. Elina and F. M. Mulinskaya.

Anode wear was estimated from the loss of weight. The anodes were boiled in distilled water for a long time after electrolysis in order to remove salt; the boiling was continued until the chloride content of the given portion of water remained at zero after several hours of boiling. The anodes were then dried to constant weight at $100-110^\circ$. All the operations were repeated; the anode weight was found to remain constant to within 0.1 g. In a number of cases greater constancy could not be achieved because of crumbling of graphite particles during the washing. This degree of precision is adequate, because the loss of weight of each anode reached several grams. The anodes were subjected to similar treatment before the experiments.

(where K_h is the hydrolysis constant, $[Cl_2] = (Cl_2) + (HClO)$ is the chlorine concentration determined by analysis (M), and γ represents the activity coefficients) we have

$$(H') = \frac{1}{2} \left\{ [H'] - \frac{K_h}{(Cl') \gamma_{H'} \gamma_{Cl'}} + \sqrt{\left\{ \frac{K_h}{(Cl') \gamma_{H'} \gamma_{Cl'}} - [H'] \right\}^2 + 4 \frac{K_h ([H'] + [Cl_2])}{(Cl') \gamma_{H'} \gamma_{Cl'}}} \right\}.$$

Since at room temperature $K_h = 4 \cdot 10^{-4}$ [1], $(Cl') \simeq 4.5$, and with the approximate value $HCl \gamma_{\pm HCl} = \sqrt{\gamma_{H'} \gamma_{Cl'}} \simeq 1.5$ [11], for the activity coefficient, we have $\frac{K_h}{(Cl') \gamma_{\pm HCl}^2} \simeq 0.4 \cdot 10^{-4}$. * Appreciable differences

between $[H']$ and (H') were only found at low acidities (less than 0.003 N).

Determinations of solution pH with a glass electrode give pH values smaller by about 0.5 unit than the values calculated from the acidity. The difference is probably due to the salt error of the glass electrode, the value of the activity coefficient of HCl, and the diffusion potential.

In some experiments the composition of the anode gas was determined by analysis of "nonchlorine gas" [12]. A modification of the known method proposed by S. S. Shraibman and N. N. Beloglazov was used. For a sharper determination of the end of chlorine absorption we previously saturated the solution used (25 g KCNS and 270 g NaCl per liter) with a mixture of CO_2 and air in 1:2 ratio (the carbon dioxide concentration in the residue after chlorine absorption was generally somewhat higher, about 40-60%; analyses in which the carbon dioxide content of the residual gas was substantially less were rejected as unreliable). It was assumed that the residue after absorption of CO_2 and O_2 was nitrogen. ** The amount of nitrogen agreed closely with the amount of oxygen, so that O_2 of electrochemical origin (not derived from the air present) did not exceed 0.01-0.02%.

The method described can give a systematic error of up to 0.1% in the CO_2 content. With low carbon dioxide contents this error is significant. Nevertheless this method gives results of the right order of magnitude, and these results can be used for comparative characterization.

RESULTS AND DISCUSSION

Data on the wear of new anodes which had not been used *** are represented in Fig. 2 by points 1, 2 (points 2 indicate the results of experiments in single-diaphragm cells). At anolyte acidities from about 0.01 N anode wear is independent of acidity. At lower acidities wear increases with fall of acid concentration, slowly at first and then very rapidly. This relationship suggests that two different mechanisms of anodic liberation of oxygen and carbon dioxide formation are involved. At $C_{HCl} > 0.01$ N (pH < 1.5) discharge of water molecules predominates; its rate is independent of pH. At lower acidities discharge of OH^- ions begins to predominate; the higher the solution pH, the more part do they take in the process.

Figure 2 shows that a threefold increase of anolyte acidity at $C_{HCl} > 0.01$ N does not influence anode wear. This is consistent with the view that water molecules are discharged; their concentration is independent of acidity.

Moreover, as Fig. 3 shows, anode wear (after subtraction of a certain constant value) in weakly acidic solutions is, in the first approximation, inversely proportional to acidity, i.e., directly proportional to the concentration of OH^- ions. This is precisely the relationship to be expected with direct discharge of OH^- ions. Water molecules are discharged at the same rate both at low and at high acidities. Therefore anode wear due to discharge of hydroxyl ions should be reckoned from the level corresponding to wear due to discharge of water molecules (Fig. 3, dash line).

* Error in estimations of the activity coefficients leads to only a small quantitative change in the calculated acidity values without introducing any significant changes into the main results.

** Hydrogen does not usually penetrate into the anode compartment in laboratory cells of the type described. Formation of CO was not observed under these conditions.

*** The NaCl concentration of the anolyte was 4.6 ± 0.3 M.

The relationship between anode wear (G g/1000 amp-hr) and acidity (H^+) is approximately represented by the expression:

$$G = 0.5 + \frac{0.94 \cdot 10^{-3}}{(H^+)}$$

Simple relationships between the partial current density for oxygen and the concentration of the discharging particles (H_2O , OH^+) may be obtained in this case because oxygen liberation occurs against a background of chlorine liberation, which ensures that the potential remains virtually constant. The high concentration of the strongly adsorbed Cl^- ion ensures an unchanged structure of the double layer with variation of the OH^+ ion concentration, as the hydroxyl ions are present in incomparably smaller amounts and are adsorbed very slightly.

The views put forward above on the mechanism of oxygen liberation are regarded by us as a working hypothesis, which must be verified by further investigations.

In Fig. 2 the data on anode wear during the second and third cycles of operation in laboratory cells are represented by points 3, and data on the wear of anodes previously used in a complete cycle under production conditions are indicated by points 4.

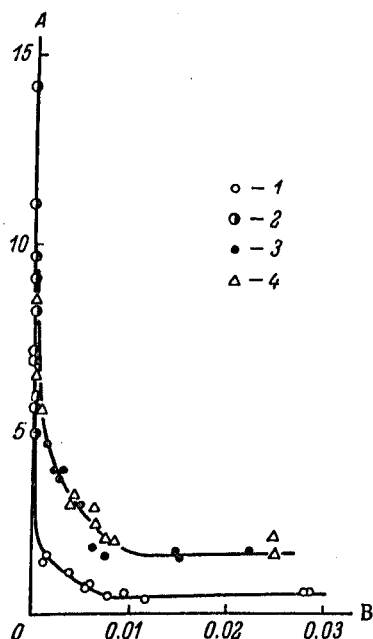


Fig. 2. Variation of anode wear with anolyte acidity. A) Anode wear G (g/1000 amp-hr); B) acidity (M).

It is clear from Fig. 2 that the relationship between anode wear and acidity is of the type described above, but the degree of wear is considerably greater. This increased wear must be attributed to increasing mechanical crumbling of the anodes. Wear of unused anodes is primarily chemical wear; i.e., it represents the loss of graphite weight due to formation of carbon dioxide. Chemical wear at high acidity, calculated from the carbon dioxide content (found to be 0.2%), is 0.45 g/1000 amp-hr, which is very close to the experimental value (average of 0.5 g/1000 amp-hr). Although the CO_2 content is not determined very precisely, there is no doubt that even allowing for possible errors these values are very close and it may be assumed that chemical wear constitutes the major part of total wear of new anodes.

The weight loss of greatly worn anodes is considerably greater than that of new anodes over the entire acidity range studied. At the same time, the CO_2 content is almost the same in both cases.* this shows that the difference in wear can be attributed only to a considerable intensification of mechanical wear.

It is probable that when a new anode takes part in electrolysis, at first there is only oxidation of surface carbon atoms, removed in the form of CO_2 , and mechanical crumbling of graphite particles begins only after the surface has become greatly loosened as the result of oxidation. Therefore, only chemical wear is observed during the first period of electrolysis, and mechanical wear does not appear until later. Loosening of the surface layer penetrates to only a small depth, and therefore subsequently mechanical wear remains almost constant. This state of affairs was first observed by Bulygin [6] during electrolysis of solutions of oxy-acids.

In our experiments anode wear was almost the same after 2-3 cycles (1-2 months) of operation in a laboratory cell under conditions of low wear as after 7-8 months of much more rapid breakdown in industrial cells. In some instances anode wear was somewhat less during the second cycle (after a relatively short first cycle). It is probable that in such cases the highly porous structure of the surface layer had not yet fully developed.

It is interesting to note that the ratio of chemical to mechanical wear is not constant but depends on the rate of graphite oxidation — mechanical crumbling of the anodes becomes relatively less with increase of chemical wear.

* The systematic error in CO_2 determination is not significant in the comparison of these two series of experiments, because the same analytical methods were used.

The ratio (K) of mechanical to chemical wear may be approximately represented, on the basis of our data, by the following equation:

$$K = 2.8 - 63x,$$

where x is the fraction of the current consumed in oxidation of the anode (with the assumption that the chemical wear G_{chem} is due almost entirely to CO_2 formation, we have $x = \frac{G_{\text{chem}}}{112}$). If chemical wear is high ($x \geq 0.03$), K becomes almost constant (about 0.8). The data are not precise enough to allow the above relationships to be regarded as a rigorous quantitative characterization of the dependence of mechanical on chemical wear. There is no doubt, however, that they can be used for approximate calculations of anode wear.

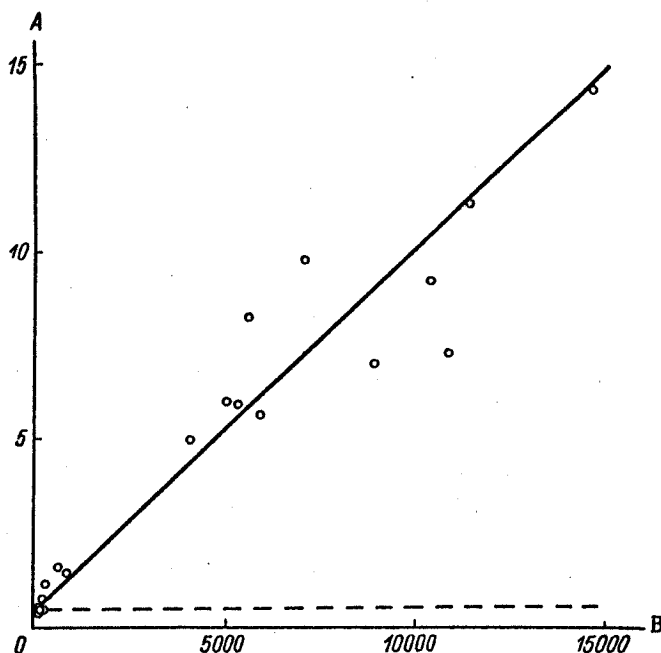


Fig. 3. Variation of the wear of new anodes with the reciprocal value of the anolyte acidity. A) Anode wear G (g/1000 amp-hr); B) $1/(\text{H}^+)$.

It is possible that this type of relationship between mechanical and chemical wear is attributable to the fact that when oxygen liberation is rapid the graphite grains are burned to a considerable extent before they can crumble away.

SUMMARY

A study of the wear of graphite anodes under the conditions of electrolytic chlorine production showed that wear is virtually constant when the anolyte acidity is above 0.01 N, while at lower acidities it increases; the increase is, in the first approximation, inversely proportional to the acid concentration. To account for this relationship it is suggested that oxygen is liberated on graphite by discharge both of OH^+ ions and of H_2O molecules. The ratio of mechanical to chemical wear of graphite depends on the absolute value of chemical wear.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
