

INFLUENCE OF IMPREGNATION ON CHEMICAL WEAR OF GRAPHITE ANODES*

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It was shown in the preceding communication [1] that an impregnant introduced into an anode has virtually no specific influence on the anode potential. The electrode potential is raised because the electrolysis process is displaced to the surface and the true current density is increased.

V. S. Ioffe, who studied simultaneous discharge of Cl^- and OH^- in concentrated NaCl and HCl solutions, showed that in the range of technical current densities the current efficiency for chlorine increases and the current efficiency for oxygen correspondingly decreases with increase of current density [2]. This result was subsequently confirmed by special investigations of the influence of current density on the relative evolution of chlorine and oxygen or on chemical wear of unimpregnated graphite [3-5]. V. S. Ioffe attributed the useful effect of impregnation to the fact that it excludes internal pores from electrolysis; within such pores the current efficiency for oxygen is considerably higher than on the surface, because of the lower true current density.

Changes in the composition of the anode gas in electrolysis of sodium chloride solutions when impregnated electrodes were used have been reported in [6-8], but this problem has not been studied in detail. In some instances there are considerable discrepancies between the results reported in these publications.

We have therefore carried out systematic investigations of the composition of the anode products and of chemical wear of impregnated anodes for different chlorine-oxygen discharge ratios.

EXPERIMENTAL

The investigations were carried out with graphite electrodes from the Dnepr Electrode Factory (DÉZ), not impregnated and impregnated with different substances, under the conditions described in the previous communication [1].

Experiments on determination of anode wear in hydrochloric acid were carried out by the method devised by V. S. Ioffe and A. V. Motsareva and improved by ourselves†. It consists of electrolysis of dilute HCl in a cell without a diaphragm (Fig. 1). Constant acid concentration was maintained in the cells by automatic dropwise supply of hydrochloric acid (concentration 100 g/liter) into each cell. The acid was fed from Mariotte vessels, the required volume of solution being displaced by hydrogen produced in auxiliary V-shaped cells with nickel electrodes by electrolysis of approximately 15% caustic soda solution. Experiments with phosphoric acid were carried out in a similar cell.

Because of the absence of flowing electrolyte in the cell, anode mud could be collected and anode wear determined.

The anode was a graphite specimen $70 \times 20 \times 20$ mm in size, with a working length of 60 mm. The anode wear was almost uniform on all four sides (for example, 1.5 mm on the cathode side, and 1.3 mm on the lateral face). The current strength, temperature, and hydrochloric acid concentration (the phosphoric acid concentration remained virtually constant during electrolysis) were determined at hourly intervals during electrolysis. The experiments were conducted at 480 A/m^2 current density and 70° for 50 h; about 125 A-h was passed through the cell. The quantity of electricity was determined with a copper coulometer.

*Communication II in the series of investigations of the protective mechanism of anode impregnation in electrolytic production of chlorine.

†This method has now been adopted as a GOST standard for graphitized anodes.

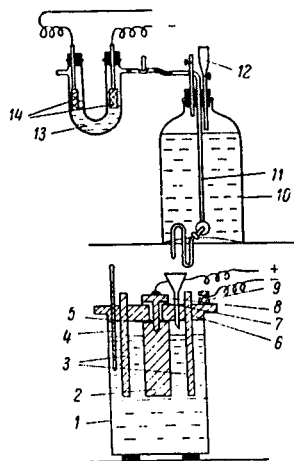


Fig. 1. Cell for determination of chemical wear in acid solutions. 1) Cell for anode tests; 2) anode; 3) cathodes; 4) thermometer; 5) rubber lining; 6) lid; 7) transparent plastic insulator; 8) head; 9) nipple and nut (parts 2, 3, 6, 8, and 9 are made of graphite); 10) feed bottle; 11) hydrogen inlet tube; 12) funnel for filling the bottle with acid; 13) auxiliary cell for hydrogen production; 14) nickel electrodes (10-14 used in experiments with hydrochloric acid).

hour before a sample was taken special care was taken to maintain the required electrolyte acidity and temperature in the cell.

Under our experimental conditions dissolved chlorine was reduced at the cathode; this was taken into account as described below. We attempted by various methods to decrease reduction, but the reproducibility of the results was adversely affected, and therefore these attempts were abandoned.

The composition of the anode gas was determined by means of the VTI-2 gas analyzer, a mixture of the anode and cathode gases being taken into the apparatus. After absorption of the individual components of the anode gas in the appropriate absorbents, hydrogen was burned out at 350° on copper oxide. The sealing liquid was saturated sodium chloride solution acidified to 0.1 N. Chlorine was absorbed in a mixture of KI and NaCl solutions. Both these liquids absorb CO₂ to some extent. The correction for CO₂ was specially determined: carbon dioxide was absorbed from a previously prepared mixture of CO₂ and N₂ with approximately the same CO₂ content as the sample, with a standard number of shakings of the apparatus. The correction was about 15% of the amount of CO₂ determined. In addition, a correction was applied for oxygen from the atmosphere, determined from the residue taken as nitrogen (with a total oxygen content in the sample ranging from 2.5 to 11 cm³, the amount of oxygen from the atmosphere was 0.5-0.8 cm³).

The amount of Cl₂ reduced at the cathode was found from the difference between the theoretical amount of H₂ and the amount actually collected during a definite time interval. The loss due to reduction of chlorine was approximately 50% of its total content. In calculation of the anodic current efficiency for chlorine the amount of chlorine reduced at the cathode was added to the amount found in the sample.

The accuracy of analysis of the anode gas in hydrochloric and phosphoric acids was checked in two ways. First, the balance of anode and cathode products in a given sample, with the current consumption taken into account, was calculated. The average discrepancy in the balance was 3-4%. Second, the chemical wear of the anode calculated from the composition of the anode gas was compared with the chemical

During the initial period of anode operation the main effect is oxidation of graphite, and mechanical wear does not yet appear. However, special experiments showed that when the degree of wear has reached 30% of the specimen weight the influence of this period may be disregarded in assessment of the total anode wear. For example, at 250 A/m² the anode wear rate at 17, 31.5, and 83% wear was 124.6, 143.2, and 143.9 g per 1000 A-h. Accordingly in determinations of the dependence of wear on current density the specimen size and operating time could be varied provided that the above condition (at least 30% wear) was satisfied.

At the end of the experiment the anode was washed in running water for 2-3 h to remove acid from the pores, and dried at 110-120° to constant weight. The decrease of anode weight during electrolysis represented the total anode wear, which was expressed in grams per 1000 A-h. Mechanical wear was found from the weight of the mud, collected on a paper filter. In experiments with phosphoric acid the weight of mud was corrected for the acid remaining on the filter; this was found by leaching of the acid from the mud and the filter. In addition the content of colloidal graphite and soluble compounds of graphite and oxygen was determined in the filtrate by coagulation by the action of concentrated hydrochloric acid; it was 0.2-0.4% of the total mud. The difference between total and mechanical wear gave the chemical wear of the anode. The reproducibility of the values for these three types of wear was 1-2 g per 1000 A-h; in some experiments the deviations reached 5 g per 1000 A-h.

At the start of electrolysis the composition of the anode gas varies appreciably owing to saturation with gases from the electrolyte. Therefore in the subsequent work only the data from the following period of operation were taken into account, when the composition of the gas was virtually constant. Since the composition of the anode gas is strongly influenced by the electrolysis conditions, during the

TABLE 1. Current Efficiencies for Anode Gases and Graphite Wear in a Solution of 5 g HCl per liter at 70°, Current density 480 A/m²

Impregnants	Number of expts.	Current efficiency (%)				Anode wear (g/1000 A-h)			
		Cl ₂	CO ₂	O ₂	CO	total	mechanical	Impregnants	
								by difference	gas analysis
15% manganese linoleate	7	51.2	34.3	10.4	4.1	71.6	24.0	47.6	47.5
15% lacquer 411	5	54.1	33.4	8.1	4.4	79.1	29.1	50.0	47.3
15% linseed oil	6	42.4	45.1	9.4	3.1	86.0	28.8	57.2	57.6
100% linseed oil	6	40.6	44.9	10.5	4.0	90.8	32.6	58.2	59.2
15% "Etinol" lacquer	5	40.4	46.4	9.5	3.7	92.5	34.4	58.1	60.4
Unimpregnated	6	38.1	48.8	7.9	5.2	123.6	56.2	67.4	66.4

wear found from the difference between total and mechanical wear. The deviation between the average values for chemical wear found from the weight and from the results of gas analysis was 1-5%. It should be noted here that the chemical wear by weight is the average value for the experiment, and is influenced by all the fluctuations of the process conditions, whereas chemical wear as given by gas analysis represents the situation at the instant of sampling. Therefore better agreement between the two values is hardly to be expected, and the agreement found should be regarded as quite satisfactory.

Determinations of total and chemical wear of anodes in sodium chloride solution (concentration 170 g/liter, acidity 0.03 N) were performed by the method described earlier [9]. Anodes which had been through a full run of industrial electrolysis were taken for the tests, because their mechanical losses were stabilized and also because separation of the impregnating substance, which occurs with fresh anodes impregnated with linseed oil, had ceased.

Preliminary experiments showed that at anolyte concentrations above 0.03 N the CO₂ content is almost constant. It may be noted that in the more concentrated NaCl solutions used industrially a constant rate of wear is attained at a considerably lower acidity [9].

Complete analyses of the anolyte and catholyte were performed every 24 h. The NaCl concentration in the anolyte was 170 ± 6 g/liter. The anolyte acidity was adjusted 2 h before the gas sample was taken. The experiment was continued for 30-40 h. The total anode wear was found from the experimental results, and chemical wear of the anode was calculated from the composition of the anode gas. The difference between the two gave the mechanical wear. It must be emphasized that the precision in determinations of mechanical wear is not high, as it was found as the difference between two large quantities, without any independent check (it is virtually impossible to collect the anode mud quantitatively in a diaphragm cell). The composition of the anode gas was found by the "nonchlorine" method [9, 10]. The discrepancies in the values found for the Cl₂ and CO₂ contents were 0.1-0.2%. However, since the CO₂ content is itself very low (0.8-1.3%), the relative error in this determination is fairly high.

EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 contains average data on the composition of the anode gas and on the loss components for impregnated and unimpregnated anodes in hydrochloric acid. Impregnation of the graphite with any of the substances tested resulted in considerable changes in the relative proportions of the anode products. The observed difference can in general be represented by two tendencies: 1) increase of the ratio of chlorine to oxygen liberated; 2) increase of the proportion of free oxygen given off, and decrease of the proportion of combined oxygen* (CO₂ and CO). The extent of the difference depends on the impregnant used. These changes in the composition of the anode gas led to considerable decreases of chemical wear; for example, by a factor of 1.4 in the case of anodes impregnated with manganese linoleate solution.

*The increase of the chlorine-oxygen ratio with impregnated anodes was observed qualitatively by F. I. Mulina and L. M. Elina in 1956.

TABLE 2. Current Efficiencies for Anode Gases and Graphite Wear in a Solution of 170 g NaCl per Liter, Acidified to 0.03 N, at 1000 A/m² and 80°

Impregnants	Number of expts.	Current efficiency (%)		Anode wear (g/1000 A-h)		
		Cl ₂	CO ₂	total	mechanical (by difference)	chemical (by gas analysis)
15% lacquer 411	3	98.15	1.85	2.76	0.71	2.05
15% linseed oil	4	98.2	1.8	2.63	0.63	2.0
Unimpregnated	4	97.6	2.4	3.83	1.13	2.7
Unimpregnated, at the potential of an impregnated anode (at 2000 A/m ²)	7	98.0	2.0	3.08	0.88	2.2

It should be taken into account that such substantial changes in the relative proportions of the anode gas components could occur only in an electrolyte in which a fairly large proportion of the current is expended for discharge of oxygen. It is quite evident that the quantitative proportions given in Table 1 apply only to the solution investigated. However, the nature of the influence of impregnation on gas composition and chemical wear should be similar for any electrolyte under conditions of competing chlorine and oxygen discharge.

In experiments with sodium chloride solution of a concentration of 170 g/liter, in which the anode process is accompanied by predominant discharge of chlorine (conditions close to industrial), impregnation altered the proportions of anode products in the same direction as in hydrochloric acid solution: the chlorine content increased and the carbon dioxide content decreased (Table 2). Similar changes in the proportions of the components of the anode gas in NaCl solution were observed earlier [6, 7].

In accordance with the views put forward by Ioffe [2], impregnation of the anode displaces the electrolysis process from the graphite pores onto the surface; i.e., the current density distribution over the depth of the electrode alters. Rise of the true current density decreases the proportion of current consumed for liberation of oxygen. The displacement of electrolysis to the surface was attributed by Ioffe to complete blocking of the pores by the impregnant.

Our investigations of the composition of the anode gas and of the polarization characteristics of impregnated graphite showed that the effect is not necessarily due to blocking of the internal pores by the impregnant. It may be obtained at a relatively low degree of pore filling, as the result of increased resistance of the electrolyte in the pores and a certain amount of shielding of the active graphite surface. The impregnating substance does not exert any appreciable specific influence on the electrode potential. Therefore the main effect of impregnation is apparently due to displacement of electrolysis from the graphite pores. Equal surface potentials should correspond to approximately equal distributions of current density over the depth of the anode and consequently to equal chemical wear.

To verify this explanation, we compared the compositions of the anode gas and the wear of impregnated and unimpregnated graphite at the same potential. In agreement with the results of our preceding investigation [1], the current density at the unimpregnated anode was roughly double that at the impregnated anode. The results are plotted in Fig. 2; they show that variations of the individual components of the anode gas with current density or potential are the same for impregnated and unimpregnated graphite. In both cases the ratio of chlorine to oxygen increases*. It is important to note that the compositions of the anode gas and chemical wear values of impregnated and unimpregnated anodes are much closer at an equal potential than at an equal geometrical current density. For example, the current efficiencies for CO₂ at an unimpregnated anode and at one impregnated with 15% linseed oil at 1.68 V potential are 48.8 and 47.8% respectively (Fig. 2), and at 480 A/m² current density they are 48.8 and 45.1% (Table 1). Thus, the explanation that the influence of impregnation on wear is due to increase of the true current density is in general confirmed. However, the respective curves do not coincide completely. Impregnation has a somewhat greater influence on chemical wear than a mere increase of current density to the same true current density at the anode surface (the same electrode potential). This may be explained as follows: the resistance of the electrolyte in the finest pores is very high because of their small cross section. Therefore the true current density is lowest in the fine pores, and consequently conditions for oxygen evolution are the most favorable.

* Similar variations of the composition of the anode gas or of chemical wear of unimpregnated graphite in narrower ranges of current density were reported in [3-5].

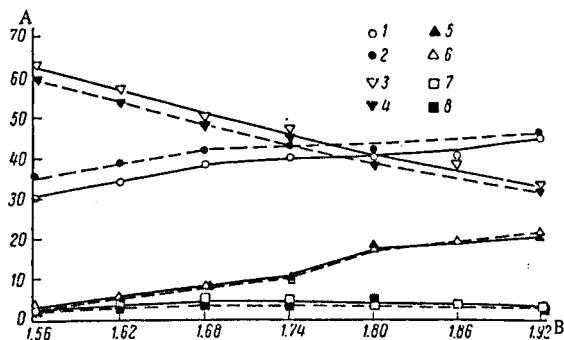


Fig. 2. Current efficiency for the anode gas as a function of the potential in a solution of 5 g HCl per liter at 70°. A) Current efficiency (%); B) potential (V). Current efficiency: 1, 2) Cl_2 ; 3, 4) CO_2 ; 5, 6) O_2 ; 7, 8) CO. Graphite: 1, 3, 6, 7) Unimpregnated; 2, 4, 5, 8) impregnated.

As the potential increases, despite the continuously increasing oxygen activity, the graphite oxidation rate begins to lag behind the increasing rate of oxygen evolution; this is especially pronounced in the region of 1.74–1.80 V.

It is possible that increase of the anode potential has a greater accelerating effect on discharge of oxygen than on the subsequent reaction of graphite oxidation.

Another possible explanation of the results obtained is that the proportion of current consumed for evolution of chlorine increases with increasing current density. Chlorine evolution has virtually no effect on the oxygen discharge rate [1], but it may retard the oxidation of graphite, which follows liberation of atomic oxygen.* In that case the decrease of the relative amount of combined oxygen and increase of the amount of free oxygen on increase of potential may be attributed to the increasing influence of the chlorine liberated. As will be shown later, under our experimental conditions chlorine does in fact have a considerable retarding effect on the oxidation reaction. It is possible that the decrease of the relative amount of CO_2 in the total oxygen on increase of the potential is due to the simultaneous influence of both the above-mentioned factors.

Thus, investigation of the influence of current density on the composition of the anode gas obtained with unimpregnated and impregnated graphite confirmed the suggestion that the influence of impregnation on chemical wear of the anode is due primarily to increase of the true current density. However, the increase of current density produced by impregnation of the graphite is more effective than would be due to a mere increase of current strength, because the current efficiency for chlorine is influenced by the degree of participation of the finest pores in electrolysis as well as by the true current density at the surface. Apparently, the differences in chemical wear with different impregnants are due to differences in the degree of participation of these pores.

Introduction of approximately equal amounts of substance into the graphite pores leads to almost equal increases of current density and potential. However, most probably the distribution of different substances in the graphite pores differs somewhat, and depends on the physical properties of the substances (viscosity, adhesion to graphite, etc.). Therefore differences of current distribution in the pores, and therefore in the relation between the individual components of the anode gas, are to be expected. Substances with the most suitable combination of physical properties probably fill the very fine pores more effectively, and this would lead to a somewhat greater decrease in chemical wear of the graphite.

Investigations of the influence of impregnation on the relative proportions of the individual components of the anode gas during simultaneous evolution of chlorine and oxygen could not give a definite answer as to whether the impregnant has any specific influence on the rate of graphite oxidation. To settle this point, experiments were carried out under conditions of discharge of oxygen only; the composition of the anode

*The retarding influence of chlorine on the rate of chemical oxidation of graphite has been observed previously [12].

Increase of the geometrical current density results in "displacement" of electrolysis from the fine pores into larger ones. This results in a decrease of oxygen evolution and in increase of the current efficiency for chlorine [11]. In an impregnated electrode the impregnant fills the fine pores to a considerable extent. Electrolysis in those pores does not merely weaken but ceases almost entirely. Therefore a large gain of current efficiency for chlorine is obtained with an impregnated anode.

The overall oxygen current efficiency falls in both cases with increase of current density. However, the ratio of free to bound oxygen varies in different ways in different regions of potential. In the region of 1.56–1.60 V, the activity of the discharging oxygen is already so high that the proportion of the current consumed for oxidation of graphite is roughly 20 times the proportion for evolution of free oxygen.

TABLE 3. Current Efficiency for Anode Gas and Graphite Wear in a Solution of 70 g H₃PO₄ per Liter at 70° and 1.78 V Potential

Impregnants	Number of expts.	Current efficiency (%)			Anode wear (g/1000 A-h)			
		CO ₂	O ₂	CO	total	mechanical	chemical	
							by difference	gas analysis
15% Mn linoleate	7	94.1	0.3	5.6	194.2	77.0	117.2	117.2
15% lacquer 411	5	92.7	1.1	6.2	200.8	82.9	117.9	117.4
15% linseed oil.	6	92.3	0.5	7.2	211.9	92.7	119.2	119.3
100% linseed oil	6	92.2	1.0	6.8	221.4	95.5	125.9	118.3
15% "Etinol" lacquer . . .	3	94.5	0.2	5.3	212.7	95.1	117.6	118.4
Unimpregnated.	5	92.8	1.4	5.8	221.1	103.8	117.3	116.8

gas was determined in a solution of 70 g H₃PO₄ per liter with the use of unimpregnated graphite, and of graphite with various impregnants.

The results, obtained at the same surface potential, are given in Table 3; they show that the composition of the anode gas is almost the same with and without the use of various impregnants; i. e., that the impregnants have hardly any influence on the ratio of free to combined oxygen. Therefore chemical wear of impregnated and unimpregnated anodes is also almost the same.*

It is interesting to compare oxidation of graphite in phosphoric and hydrochloric acid at the same potential (i. e., at the same partial current density for oxygen). The proportion of CO₂ in the total oxygen at 1.78 V potential is 92% in H₃PO₄ and 71% in HCl (calculated from Fig. 2). Therefore evolution of chlorine clearly retards oxidation of graphite by oxygen. Accordingly, two factors decreasing the proportion of combined oxygen with increase of the potential may become more pronounced: first, increase of the proportion of chlorine intensifies retardation of the oxidation; second, at a lower oxidation rate the lag of oxidation behind the increasing rate of oxygen evolution becomes more pronounced.

Changes in the relative proportions of free and combined oxygen become noticeable only at a high potential. At the anode potential of the industrial chlorine cell (below 1.5 V) almost all the oxygen is combined as CO₂ and the proportion of the other products (O₂ and CO) is very small. This result is fully consistent with the findings of Vaaler [7], who reported that the contents of CO and O₂ in chlorine are much lower than the CO₂ content. Therefore changes in the relative amounts of chlorine and oxygen liberated are of decisive significance for the effect of anode impregnation in industrial cells.

The data in Table 2 show that in electrolysis of NaCl impregnation does in fact decrease the proportion of CO₂ considerably. Most of the effect is due to displacement of electrolysis from the pores to the surface, and a small additional effect is due to displacement of electrolysis from the fine pores. This is clear from the data for an unimpregnated anode at the potential of an impregnated one: its chemical wear is considerably lower, but is still somewhat higher than that of the impregnated anode.

Tables 1-3 also contain data on mechanical wear of anodes, i. e., on weight losses due to crumbling of separate particles. This wear component is also considerably less for impregnated anodes, and is not proportional to chemical wear.

CONCLUSIONS

1. It is shown that impregnation of graphite leads to an increase in the ratio of chlorine to oxygen. Chemical wear decreases with increase of the true current density, owing both to displacement of electrolysis to the anode surface and to blocking of fine pores.

The differences in the effects of different impregnants are attributed to differences in the distribution of the substances in the anode pores, leading to different distribution of current density across the anode.

2. It is shown that the chemical activity of anodic oxygen is not diminished to any appreciable extent in presence of impregnants in the graphite pores.

*The somewhat greater chemical wear of the anode impregnated with 100% linseed oil is probably attributable to inaccurate determination of the total wear and therefore of chemical wear, due to separation of oil. The composition of the anode gas did not show any peculiarities.

3. During simultaneous discharge of chlorine and oxygen, chlorine has a retarding effect on oxidation of graphite.

LITERATURE CITED

1. F. Mulina, L. Krishtalik, and A. Kolotukhin, *ZhPKh*, 38, 2807 (1965).
2. V. Ioffe, *ZhKhP*, 13, 668, 784 (1936).
3. T. Filipov, A. Motsareva, and V. Grinevich. Abstracts of Papers at the Fourth Electrochemical Conference [in Russian], 98 (1956).
4. N. Nechiporenko, P. Voroshilov, N. Sivokon', and V. Beidin, *ZhPKh*, 33, 1818 (1960).
5. B. Bulygin, *ZhPKh*, 31, 1832 (1958).
6. L. Krishtalik, G. Melikova, and E. Kalinina, *ZhPKh*, 34, 1543 (1961).
7. Vaaler, J. *Electroch. Soc.*, 8, 691 (1960).
8. M. Flisskii, I. Veselovskaya, and R. Dzhagatspanyan, *ZhPKh*, 33, 1901 (1960).
9. L. Krishtalik, G. Melikova, and E. Kalinina, *ZhPKh*, 34, 1537 (1961).
10. S. Shraibman. Control of the Production of Chlorine and Caustic by Electrolysis of Common Salt [in Russian]. Goskhimizdat, Moscow-Leningrad (1934).
11. O. Ksenzhek and V. Stender, *DAN SSSR*, 107, 280 (1956).
12. G. R. Hennig. Proceedings of the Fourth Conference on Carbon, 145 (1960).

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.
