

INFLUENCE OF IMPREGNATION ON MECHANICAL WEAR OF GRAPHITE ANODES DURING ELECTROLYTIC PRODUCTION OF CHLORINE*

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Oxidation of graphite by oxygen liberated at the anode decreases the size of the grains and destroys the bonds between them, and as a result part of the anode material crumbles away in the form of mud. This part of the loss is usually described as mechanical wear. The present communication deals with the influence of impregnation on this component of wear.

EXPERIMENTAL

In investigations of the influence of impregnation on anodic destruction of graphite, mechanical wear was determined in addition to chemical wear. The experimental procedure was described in the preceding communication [1].

The particle-size composition of the anode mud was determined by sedimentometric analysis [2]; the mud was first separated into four fractions with the aid of Sabanin's devices. Mixtures of ethyl alcohol, which wets graphite well, with glycerol were used as the dispersion media. The solution viscosities were so chosen that the sedimentation rate of even the largest particles corresponded to the region where the law of Stokes is valid. The following glycerol-alcohol mixtures were used: 40% solution of glycerol in alcohol for the coarse fraction, 25% solution for the medium fraction, 5% for the fine fraction, and pure alcohol for the residue. Data for all four fractions were added for plotting the differential curve of particle distribution by size.

In investigations of mechanical wear, about 15 different substances were tested as impregnating materials in addition to those indicated earlier [3]. Most of the investigations were conducted in hydrochloric acid solution containing 5 g of the acid per liter.

Data on stability of graphite anodes impregnated with different substances are summarized in Table 1. These data show that impregnation of anodes with substances of the most diverse nature diminishes both chemical and mechanical wear.

Figure 1 shows the relation between the effects of impregnation† on chemical and mechanical wear in hydrochloric acid solution. Despite the specific influence of the impregnating agent (viscosity, wettability of graphite, chemical resistance of the film, and its adhesion to graphite) there is an undoubted similarity in the behavior of anodes impregnated with different materials: mechanical wear is reduced more rapidly than chemical wear by impregnation. This increase of the ratio of chemical to mechanical wear as the result of impregnation of anodes was also observed by us in other electrolytes [1]. In sodium chloride solution the impregnation effect on chemical wear was in the range of 1.33-1.36, and on mechanical wear, 1.59-1.71.

In phosphoric acid, despite the equal chemical wear of unimpregnated and impregnated anodes, mechanical wear was considerably less after impregnation. This shows that reduction of mechanical wear after impregnation of anodes is not only associated with a decrease of chemical wear but is also to some extent independent of it.

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†The impregnation effect was the ratio of the wear of an unimpregnated to an impregnated anode.

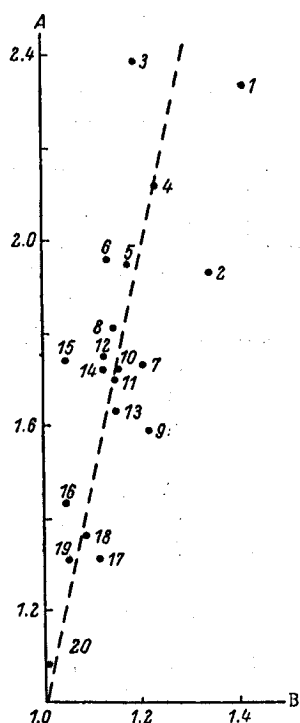


Fig. 1. Relation between the effects of impregnation on mechanical and chemical wear of graphite with different impregnating agents. A) Effect on mechanical wear; B) effect on chemical wear. The point numbers correspond to the specimen numbers in Table 1.

retained in the finer pores by capillary forces. The procedure for impregnation of anodes with 100% linseed oil does not involve removal of excess oil from the pores, but merely gives partial removal of oil from the outer pores of the graphite. As the anode wears away during electrolysis, oil is displaced by the electrolyte from the outer pores [4] and here again the larger pores are probably cleared first, because the oil is retained more firmly in the fine pores (contact regions) by the action of capillary forces. Thus, with any correctly chosen impregnation treatment the impregnating agent accumulates mainly in the finer pores and protects the regions of grain contact.

These views on the distribution of the impregnating agent in the anode pores are confirmed by the following experimental data.

Our investigations have shown [3] that impregnation with 15% solutions of various agents results in a small increase of anode potential, corresponding to doubling of the geometrical current density. The specific surface of the graphite, calculated by the formula of Ksenzhek and Stender [5], decreases in the ratio of 1.3 to 1. This semiquantitative estimate suggests that the surface of the large pores remains mostly free for ion discharge after such impregnation. If the impregnating agent covered the pore surfaces with a continuous film, the resultant rise of potential would be as sharp as if the pores were completely clogged.

It is important to note that, as our measurements of electrolyte resistance in the pores showed [3], impregnation of the anode results in a substantial increase of the coefficient of pore convolution (from 2.8 to 4.1). The most logical explanation of this fact is that the impregnating agent fills a considerable proportion of the narrow channels connecting the larger cavities in the anode [6], and as a result the path of the current in the pores becomes considerably more complicated and longer.

The explanation that the considerable reduction of mechanical wear is caused by cementing of the graphite grains by a film of the impregnating material proved to be unjustified, because with impregnating agents which are liquid under the electrolysis conditions, such as paraffin and chloroparaffin, the impregnation effect on mechanical wear is even greater than with solid substances which form strong films in the pores (Etinol lacquer, Bakelite lacquer, polystyrene). We believe that an explanation of this general effect is that the impregnating agent, distributed through the pores of the graphite by the action of capillary forces, is concentrated mainly in the fine pores, and in particular in the narrow crevices between the grains, immediately adjacent to the points of contact, and thereby protects these points against oxidation by anodic oxygen. As the result of such protection deeper oxidation of the graphite is required for separation of two grains, as contact between them can be broken only after the oxidation front has passed around the region protected by the impregnating agent. This is shown schematically in Fig. 2. It should also be noted that material which is less resistant to oxidation, formed by graphitization of the binder, is concentrated in the regions of contact between the grains. Protection of these vulnerable regions gives an additional gain of stability.

In our opinion, accumulation of the impregnating agent in the fine pores occurs as follows. When the anode is impregnated with unsaturated solutions of various substances in volatile solvents its pores are completely filled with the solution. During the drying the solvent evaporates, and as the solution tends to saturation it is displaced by the action of capillary forces from the larger to the finer pores, and the impregnating agent becomes concentrated in the remaining volume, i.e., in the finer pores. Naturally, it largely remains there after all the solvent has evaporated.

When the anode is impregnated with a substance not in a solvent (e.g., linseed oil or paraffin), the pores also become completely filled. During the subsequent removal of excess impregnating agent the larger pores again are the first to become free from the agent, while it is

TABLE 1. Relation between Chemical and Mechanical Wear of Anodes, Impregnated with Various Materials, in 5 g/liter HCl Solution at 480 A/m² and 70° (The weight increase was 2-3% with all the impregnating materials listed except 100% linseed oil and 15% paraffin)

Specimen No.	Impregnating material	Anode wear (g per 1000 A-h)			Impregnation effect on wear	
		total	mechanical	chemical	mechanical	chemical
1	15% Mn linoleate in CCl ₄	71.6	24.0	47.6	2.34	1.42
2	15% lacquer 411 in CCl ₄	79.1	29.1	50.0	1.93	1.35
3	15% lacquer 458 in CCl ₄	79.8	23.5	56.3	2.39	1.20
4	15% lacquer M-16	81.0	26.5	54.5	2.12	1.24
5	15% linseed oil in CCl ₄	86.0	29.8	56.2	1.89	1.19
6	15% seal oil in CCl ₄	87.7	28.8	58.9	1.96	1.14
7	30% tung oil in CCl ₄	88.5	32.6	55.9	1.73	1.21
8	15% chloroparaffin in CCl ₄	89.6	31.0	58.6	1.81	1.15
9	16% tung oil in CCl ₄	90.6	35.4	55.2	1.59	1.22
10	100% linseed oil*	90.8	32.6	58.2	1.72	1.16
11	15% stearin in CCl ₄	91.5	33.0	58.5	1.70	1.15
12	15% whale oil in CCl ₄	91.7	32.1	59.6	1.75	1.13
13	15% Etinol lacquer in xylene	92.5	34.4	58.1	1.63	1.16
14	100% paraffin†	92.3	32.7	59.6	1.72	1.13
15	14% lacquer 350 in CCl ₄	96.2	32.3	63.9	1.74	1.05
16	Chlorinated linseed oil in 1:1 dilution with CCl ₄	103.3	39.3	64.0	1.43	1.05
17	13% polystyrene in benzene	103.0	42.8	60.2	1.31	1.12
18	25% Bakelite lacquer in ethyl alcohol	103.3	41.4	62.1	1.36	1.09
19	24% silicone lacquer 3-9 in toluene with 6% siccativ	106.4	42.9	63.5	1.31	1.06
20	15% paraffin in CCl ₄ ‡	119.3	52.2	67.1	1.08	1.01
21	Unimpregnated anode	123.6	56.2	67.4	1	1

*Impregnated by Ipatov's method, weight increase 10%.

† Excess paraffin removed by heating

‡ Not optimum impregnation conditions; weight increase 0.5%.

Data on the influence of potential on chemical and mechanical wear are presented in Table 2.

In the case of an unimpregnated anode the electrolyte is gradually displaced from the finer pores as the potential increases, and the chemical wear approaches that of an impregnated anode. The proportion of mechanical wear (which, as was shown above, is associated to a considerable extent with oxidation of graphite near the regions of grain contact) decreases considerably. Indeed, the data in Table 2 show that the ratio of chemical to mechanical wear increases appreciably with rise of potential to 1.8 V in the case of an unimpregnated anode. Moreover, in the case of an impregnated anode, where crevices between the grains are largely excluded from electrolysis at all potentials, mechanical wear is substantially less and its relative proportion does not decrease appreciably with rise of potential. The increase of mechanical wear of graphite, both with and without impregnating agent, in the potential range of 1.86-1.92 V, accompanied by continuing decrease of chemical wear, is probably due to formation of oxide phases, and in particular of graphite oxide, which causes swelling of the graphite. This results in a sharp change in the ratio of chemical to mechanical wear. In hydrochloric and phosphoric acid solutions a sharp rise of potential occurs in the corresponding potential range [3]. These data lead to the conclusion that a potential in the region of 1.9 V represents the limit of applicability of both impregnated and unimpregnated graphite anodes.

The above explanation of the influence of electrolysis in fine pores on the stability of unimpregnated anodes is in agreement with the data of Kuchinskii, Lipikhin, and Flisskii [7], who showed that graphite anode specimens undergoing less wear loss have a smaller volume of fine pores.

TABLE 2. Influence of Potential on Wear of Graphite Anodes in 5 g/liter HCl Solution at 70°

Anode characteristics	Current density (A/m ²)		Potential†	Anode wear (g per 1000 A-h)			Ratio of chemical to mechanical wear
	initial	final*		total	mechanical	chemical	
Unimpregnated	235	295	1.62	142.0	66.1	75.9	1.16
	480	610	1.68	123.6	56.2	67.4	1.20
	910	1315	1.74	105.4	43.4	62.0	1.43
	1835	2940	1.80	92.5	38.2	54.3	1.42
	4290	6600	1.86	82.5	35.7	46.8	1.31
	6360	10000	1.92	78.3	43.7	34.6	0.79
Impregnated with 15% linseed oil	115	145	1.62	106.2	37.3	69.0	1.86
	230	285	1.68	101.3	35.2	66.1	1.88
	480	570	1.74	86.0	29.8	56.2	1.88
	890	1320	1.80	83.0	29.8	53.2	1.78
	1700	2330	1.86	78.6	28.3	50.3	1.77
	3740	5210	1.92	82.4	42.1	40.3	0.89

* The anode potential rose by 0.02–0.03 V at the end of the experiment owing to the change of current density. The sole exception is the last line in the table for the unimpregnated anode, where the current density reached a value corresponding to a sharp rise of potential [3]. In this case the final potential was about 0.2 V above the initial value.

† The current density rose at the end of the experiment owing to wear of the anode.

TABLE 3. Wear of Baked Electrodes in 5 g/liter HCl Solution at 480 A/m² and 70°

Electrode characteristics	Anode wear (g per 1000 A-h)			Impregnation effect on wear	
	total	mechanical	chemical	mechanical	chemical
Baked, unimpregnated	291.2	210.1	81.1	—	—
Baked, impregnated with 15% linseed oil	214.5	138.5	76.0	1.52	1.07

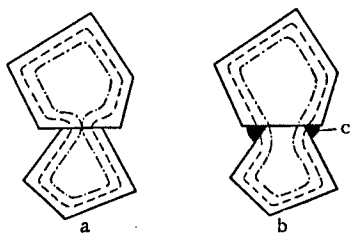


Fig. 2. Schematic diagram of a) oxidation of unimpregnated and impregnated graphite at contact regions. a) Unimpregnated graphite; b) impregnated graphite; c) impregnating agent. The broken and dot-dash lines represent schematically the gradual advance of the oxidation front.

The hypothesis of protection of the regions of contact between the grains is also confirmed by other data. Naturally, breakdown of contacts between the grains, leading to crumbling, is the last stage in mechanical destruction. At the initial stage breakdown of these contacts leads to changes in the physical properties (strength and specific resistance) of the graphite.

We determined the open-pore porosity and specific resistance of DEZ anodes impregnated with various substances, taken from 60 BGK-17 cells after operating cycles at various current densities.

Increases of porosity and specific resistance of impregnated and unimpregnated graphite after an operating cycle are compared in Fig. 3. Each point represents the average results of two or three determinations. These data show that for a given increase of porosity during electrolysis the increase of specific resistance is less in the case of impregnated anodes. Since the porosity increase is the same in both, the decrease of the mass of conducting material (graphite) is the same in both cases.

Therefore the smaller increase of specific resistance in the case of impregnated anodes can only be explained on the assumption that the contact points between the grains, which conduct the current, are protected.

TABLE 4. Influence of Impregnation after Graphitization on Wear Resistance of Different Types of Anodes in 5 g/liter HCl Solution at 480 A/m² and 70°

Graphite make	Anode characteristics	Anode wear (g per 100 A-h)			Specimen
		total	chemical	mechanical	
DÉZ	Industrial: impregnated	82.6	55.3	27.3	Impregnated before graphitizing
	unimpregnated	123.7	72.6	51.1	
	Experimental: impregnated	70.4	45.1	25.0	Not impregnated before graphitizing
	unimpregnated	135.5	70.5	65.0	
NÉZ	Industrial: impregnated	71.4	48.9	22.5	Impregnated before graphitizing
	unimpregnated	136.7	73.7	65.0	
	Experimental: impregnated	84.5	57.0	27.5	Not impregnated before graphitizing
	unimpregnated	113.4	72.4	41.0	
ChÉZ	Industrial: impregnated	90.0	58.0	32.0	Impregnated before graphitizing
	unimpregnated	150.3	74.1	76.2	

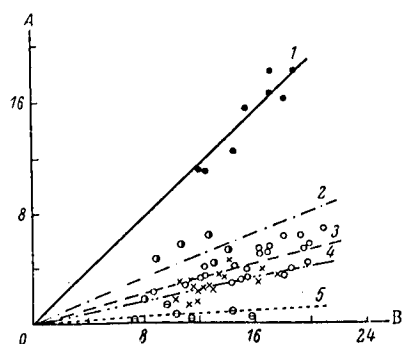


Fig. 3. Variations of specific resistance and porosity of graphite anodes during an operating cycle in a BGK-17 cell. A) Increase of resistance ($\Omega \cdot \text{mm}^2/\text{m}$); B) increase of porosity (%). 1) Unimpregnated graphite; 2,3,4,5) graphite impregnated with 15% solutions of Etinol lacquer, linseed oil, lacquer 411, and manganese linoleate.

order to break down the bond between an individual grain and the anode, the oxidation front must pass around the protected contact region; i.e., it must pass through the grain itself, destroying it. As a result the crumbling particles should be finer than in the case of unimpregnated graphite. This is conformed by the results of sedimentometric analysis of anode mud from unimpregnated and impregnated graphite (Fig. 4). A distinct shift toward a smaller particle size can be seen in the case of the mud from the impregnated anode. If the decrease of crumbling had been the result of bonding of the particles by the impregnating agent, the particle size in the mud would have been larger. The more rounded shape of the grains, observed in microscopic studies of the mud, is also the consequence of the higher degree of oxidation of the crumbled grains.

tained. However, since it is possible to continue the use of impregnated anodes to smaller residual weights, their porosity ultimately becomes approximately the same as that of unimpregnated anodes. It was found during the industrial tests that impregnated anodes have considerably higher mechanical strength than unimpregnated ones. This also indicates that the regions of contact between the graphite grains are preserved better, and accordingly the mechanical strength is retained to a greater extent.

Comparison of the wear of ungraphitized baked electrodes before and after impregnation also indicates that the regions of contact are effectively protected from oxidation by the impregnating agent (Table 3).

In this case the explanation of the distinct influence of impregnation on mechanical wear is that a baked electrode consists of numerous fine grains of irregular crystalline form, bonded by almost amorphous binder; therefore it contains more regions of contact and they are oxidized more easily than in a graphitized electrode.

As already stated, our hypothesis of the protection of regions of contact between the graphite grains by the impregnating agent involves the assumption that after impregnation in

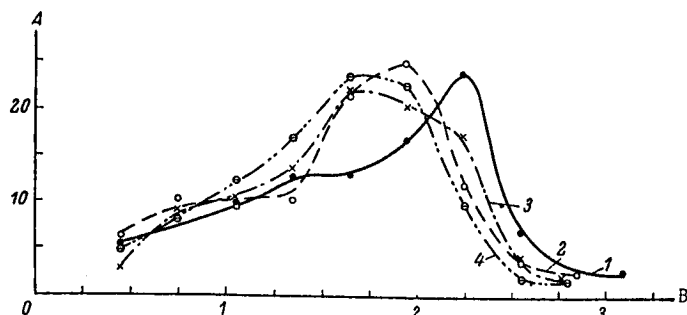


Fig. 4. Composition of anode mud from graphite in 5 g/liter HCl solution. A) Relative content of fraction in mud (%); B) log particle radius (r in μ). 1) Unimpregnated graphite; 2,3,4) graphite impregnated with 15% solutions of linseed oil, lacquer 411, and manganese linoleate.

Thus, data obtained by different methods confirm that the impregnating agent protects the regions of contact between the grains. It was concluded from this that anodes for electrolytic chlorine production need not be impregnated with oil pitch before graphitization if they are impregnated with oils or resins when graphitized. Second impregnation with nonconducting substances protects the regions of contact between the grains more reliably than first graphitization by easily oxidized carbonaceous material. The results of laboratory tests on anodes from three Soviet factories, DÉZ, NÉZ, and ChÉZ, with and without impregnation before graphitization confirmed this (Table 4).

It has now been confirmed by industrial electrolysis that impregnation of anodes before graphitization can be omitted if they are impregnated afterwards.

CONCLUSIONS

1. Impregnation decreases mechanical anode wear considerably more than chemical wear. This is attributed to protection of the regions of grain contact by the impregnating agent against oxidation; this explanation was confirmed by a number of independent methods.

2. On the basis of the view that impregnation protects the regions of contact between the graphite grains it is shown that the technological stage of electrode impregnation before graphitization may be omitted.

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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 the first issue of this year.
