

POLARIZATION CHARACTERISTICS OF IMPREGNATED AND UNIMPREGNATED GRAPHITE ANODES*

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Impregnation of graphite electrodes with various nonconducting substances is one of the commonest and most important methods of improving the stability of anodes in electrolytic chlorine production. Numerous formulations have been proposed for impregnation (e.g., [1]) but they were devised quite empirically. The main concepts on the mechanism of impregnant action, and on the mechanism of oxidation of graphite anodes in general, were formulated by Ioffe [2].

According to Ioffe, the true current density falls rapidly with increasing distance from the external surface of the anode. This is due to the ohmic drop of potential in the electrolyte contained in the graphite pores.

The true current density at the anode surface and especially within the anode is considerably lower than the apparent (geometrical) current density. On the other hand, the equilibrium oxygen potential is lower than the chlorine potential, and therefore decrease of current density, i.e., decrease of the anode potential, favors discharge of oxygen relatively to chlorine, i.e., intensifies anode wear. Impregnation prevents access of current into the internal pores. The true current density therefore rises, and the proportion of the current expended in oxygen discharge decreases.

Although this explanation is, in general, consistent with the observed process characteristics, many important questions remain unanswered. This applied, in particular, to the action of impregnants which do not fill completely the internal anode pores, to the influence of impregnation on the relation between chemical and mechanical wear (i.e., oxidation and crumbling of graphite grains), and to certain other problems.

The aim of our investigations was to investigate the mechanism of protective action due to impregnation, in order to find a basis for rational impregnation methods.

METHOD OF INVESTIGATION

The experiments were carried out with specimens of graphite electrodes from the Dnepr Electrode Factory taken from the same batch.

The specific resistance of each specimen was determined; the results were in the range of 7.5-9.5 $\Omega \cdot \text{mm}^2/\text{m}$.

Substances of different types were used as impregnating materials: linseed oil, manganese linoleate, asphalt-bitumen lacquer 411, and a number of other substances (drying oils, polymers, and hydrocarbons). As a rule, 15% solutions in a volatile organic solvent (carbon tetrachloride) were used for impregnation. In addition, two impregnation treatments with 100% linseed oil were tested (the standard treatment [1], and treatment without subsequent chlorination of the impregnated anode).

The following electrolytes were chosen for the investigation: a) hydrochloric acid, concentration 5 g/liter (for conditions of approximately equal amounts of discharging chlorine and oxygen); b) phosphoric acid, concentration 70 g/liter (for conditions of discharge of oxygen only, at pH close to that of the first solution); c) sodium chloride solutions, concentration 170 g/liter at 0.03 N acidity, and concentration 270 g/liter at 0.001 N acidity (for conditions of predominant chlorine discharge; the latter solution is similar

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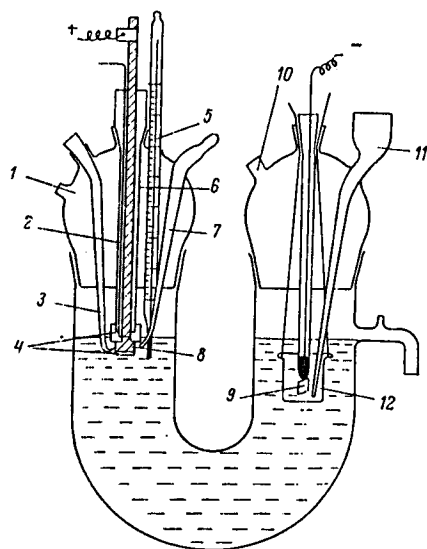


Fig. 1. Electrolytic cell for determination of polarization curves. 1) Anode gas outlet; 2) tantalum contact between graphite and the potentiometer lead; 3) electrolytic bridge; 4) polytetrafluoroethylene sleeve and disk; 5) thermometer; 6) glass tube; 7) electrolyte feed tube; 8) graphite anode; 9) platinum cathode; 10) cathode gas outlet; 11) acid feed tube for neutralization of the alkali formed; 12) beaker for alkali neutralization (11 and 12 are used in experiments with NaCl).

alkali formed was neutralized by acid directly at the cathode surface. The cathode was placed in a small beaker into which the required amount of acid was fed continuously.

A calomel half-cell was used as the reference electrode. The potential was converted to the hydrogen scale. The thermo-emf arising because the temperature of the calomel electrode was 20–22° and that of

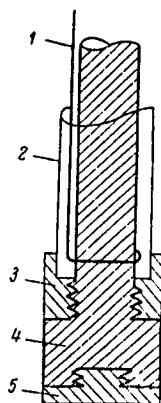


Fig. 2. Construction of the graphite anode. 1) Tantalum contact; 2) glass tube; 3) polytetrafluoroethylene sleeve; 4) graphite anode; 5) polytetrafluoroethylene disk.

to the anolyte in industrial cells). The experiments were conducted in a glass U-shaped cell (Fig. 1). The material for the inserts and interlayers was polytetrafluoroethylene. The use of rubber and various cements was excluded. The anode was a graphite rod, the bottom part of which, over a region 5–8 mm in length, was the working surface. The extent of the working surface was limited by means of polytetrafluoroethylene sleeves and disks (Fig. 2). A graphite anode 10 mm in diameter was used for the solutions of acids. This size was chosen as the result of preliminary experiments, which showed that further increase of the anode diameter has virtually no influence on the potential.

A graphite anode 5 mm in diameter was chosen for sodium chloride, because under these conditions electrolysis penetrates to a depth much less than 1 mm [3]. The current lead for potential measurements was a tantalum strip inserted by its pointed end into the graphite a few millimeters from the working surface.

Before each experiment the potential drop in the tantalum contact was determined. In addition, the distance between the anode and the electrolytic bridge was determined with the aid of a binocular magnifying glass fitted with a graduated eyepiece. It varied in the range of 0.1–0.3 mm. The potential drop in the electrolyte was calculated from Kabanov's formula [4].

The ohmic corrections, proportional to the current density, were 0.03–0.05 V at 1000 A/m² at the maximum distance for acid solutions; for NaCl solutions they were about one tenth of this.

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In preliminary work on the method it was found that the potential is substantially influenced by the duration and conditions of preliminary treatment of the anode with applied current. Establishment of a constant potential is apparently associated both with growth of the graphite surface and with changes of its state [5].

The following conditions of preliminary electrolytic treatment of graphite were chosen for the electrolyte solutions studied: for acid solutions, 17 h at 250 A/m²; for sodium chloride solutions, 70 h at 1000 A/m².

After this treatment the potential remained virtually constant with time. The direct and reverse polarization curve was determined for each specimen, the potential being measured at current densities from 1000 to 25 A/m² and then from 25 to 10000 A/m². In general, the difference between the poten-

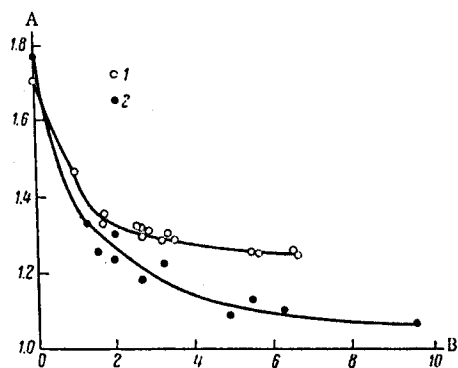


Fig. 3. Distribution of potential with depth of graphite anodes in a solution of 5 g HCl per liter. A) Potential (V); B) distance from anode surface (mm). Graphite: 1) Unimpregnated; 2) impregnated with 15% linseed oil.

sides of polarized graphite plates of different thickness (from 1 to 10 mm). The true current density was somewhat higher in polarization of thinner plates. However, the advantage of this method was that there was no question of any influence of channels on current distribution. The two methods give similar results. The data reported below were obtained by the first method. Other anode characteristics determined were the porosity (open pores) [1], the coefficient of pore convolution by the method in [7, 8], and gas permeability. The latter was characterized by the rate of flow of air through a specimen 15 mm in diameter and 30 mm thick under a pressure difference of 60 mm.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 represents distribution of potential at different depths in an unimpregnated anode and in an anode impregnated with 15% linseed oil solution. The potential on the surface of the impregnated anode is somewhat higher, but decreases more rapidly with depth and reaches lower values than in the unimpregnated anode*. This result is similar to that obtained by Ioffe [2] for an anode impregnated with 100% linseed oil. Ioffe attributed the sharp fall of potential in the impregnated anode to complete blocking of the internal pores by linseed oil. However, this explanation is not applicable to our case, because most of the pores remain open over the entire depth of the anode. This follows directly from data on gas permeability. The air flow rate through the unimpregnated anode under the conditions specified above was about 70 ml/min, through anodes impregnated with 15% solutions of various substances, and only in the case of anodes impregnated with 100% linseed oil was it as low as 0.01-0.2 ml/min.

After impregnation with 15% solutions the porosity of the graphite falls from 16-18 to 11-13%; i.e., most of the pores remain unfilled. This is to be expected, because during impregnation with a solution the pores are at first completely filled, but later most of the solvent is removed. In contrast, impregnation with pure linseed oil results in almost complete filling of the pores. Further treatment of the anode (chlorination) leads to displacement of oil from the surface pores. Therefore such anodes are impermeable to gases and have low porosity (about 4%).

Since the greater proportion of the pores remains open with most impregnating solutions, the more rapid fall of potential within the impregnated anode cannot in this case be attributed to almost complete filling of the pores. The sharper fall of potential with increasing depth is probably due to increase of the electrical resistance of the electrolyte within the pores. The increase of electrolyte resistance is due to two causes: decrease of the total cross section, and increase of the coefficient of pore convolution. The average values of the latter were found to be 2.8 for unimpregnated graphite, and 4.1 for graphite impregnated with 15% linseed oil solution. Changes of these two factors lead to an approximately threefold increase of electrolyte resistance in the pores.

*The data in Fig. 3 refer to HCl solution at 1000 A/m² current density. Similar results were obtained at other current densities, and in H₃PO₄ solution.

tials in the direct and reverse curves was 0.005-0.01 V; in less successful experiments it was 0.02 V.

In the case of impregnation with 100% linseed oil, the oil liberated after preliminary electrolytic treatment was wiped off the anodes before determination of the polarization curves. High and unstable potentials are obtained if the oil is not removed from the anode surface.

Apart from determinations of the polarization curves, some auxiliary determinations were carried out. Variations of the potential with depth in the working anode were determined. Two methods were used for this purpose. By the first method, analogous to the method of Ioffe [2] and Bulygin [6] the potential at the bottom of channels drilled in the anode was determined. In order to avoid irregularities of current distribution due to the presence and mutual influence of the channels. A large anode was used (80 × 40 mm in cross section and 40 mm long), and the distance between channels of different depth was much greater than their diameter (2 mm). In the other method the potentials were measured from the reverse

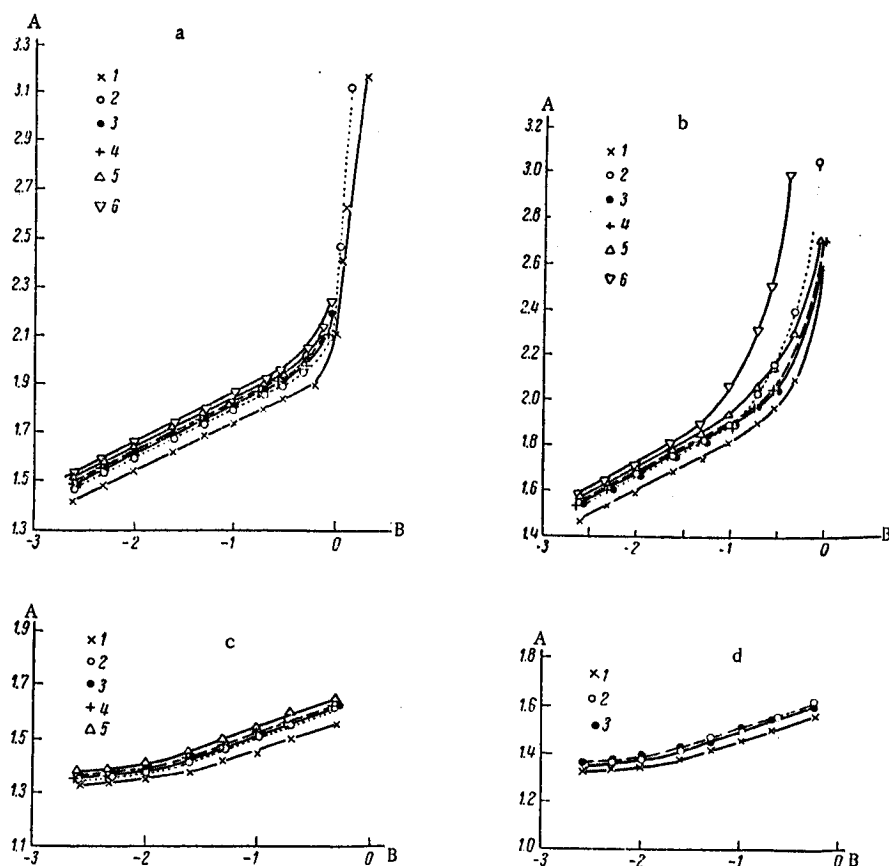


Fig. 4. Polarization curves for graphite anodes in solutions of various electrolytes at 70°. A) Potential (V); B) $\log D_a$ (A/cm^2). Electrolytes (g/liter): a) HCl, 5; b) H_3PO_4 , 70; c) NaCl, 170 (acidity 0.03 N); d) NaCl, 270 (acidity 0.001 N). 1) Unimpregnated graphite; impregnated with: 2) 15% linseed oil; 3) 15% Mn linoleate; 4) 15% lacquer 411; 5) 100% linseed oil (standard treatment); 6) 100% linseed oil (without subsequent chlorination).

Figure 4a shows that the polarization curves for impregnated anodes in hydrochloric acid solution are fairly close together and lie somewhat above the curve for unimpregnated graphite. The curves for anodes impregnated with 15% solutions almost coincide, and lie below curves for anodes impregnated with 100% linseed oil. The rise of potential is 0.05–0.07 V as the result of impregnation with dilute solutions, and 0.09–0.11 V in the case of pure linseed oil. Up to potentials of 1.9–2.0 V the course of the curves is of the Tafel type, with the same slope factor b , 0.20 V, for impregnated and unimpregnated graphite. When a potential of 1.9–2.0 V is reached the course of the curves alters.

The relative positions and nature of the curves for phosphoric acid solutions (Fig. 4b) are similar. The curves deviate from a linear course at the same potential (1.9–2.0 V).

The curves for sodium chloride solutions (Fig. 4 c, d) take a similar course. At low current densities their slope is small and they almost merge at potentials close to the equilibrium value. The linear regions begin at a current density of about $250 A/m^2$, and beyond this the curves for unimpregnated and impregnated graphite are parallel, with a slope of 0.14 V. A slope of 0.14 V for a porous electrode corresponds to one of 0.07 V for a smooth electrode [9]. A similar value for the slope at a lower temperature was also reported in [10], where it was attributed to barrier-free discharge of chloride ions (the theoretical value of b for this process at 70° is 0.068 V). The difference between the potentials of unimpregnated anodes and anodes impregnated with 15% solutions is 0.03–0.05 V; in the case of impregnation with undiluted linseed oil it is 0.07–0.09 V.

Comparison of polarization curves for different conditions of chlorine and oxygen discharge shows that in all the electrolytes studied, impregnation with 15% solutions produces only a slight increase of the

TABLE 1. Anode Potentials in HCl and H₃PO₄ Solutions at Equal Current Densities for Oxygen

Type of anode impregnation	HCl (5 g/liter)		H ₃ PO ₄ (70 g/liter)	
	current efficiency for oxygen (%)	anode potential (V), $D_a = 480 \text{ A/m}^2$	D_a corresponding to partial D_a for O ₂ in HCl	Anode potential (V)
Unimpregnated.	61.9	1.68	298	1.69
15% Mn linoleate.	48.8	1.74	221	1.74
15% lacquer 411	45.9	1.75	235	1.75
15% linseed oil.	57.4	1.74	276	1.76
100% linseed oil	59.4	1.78	286	1.80

graphite potential, and the curves for different impregnants almost coincide. It may be said that introduction of approximately equal amounts of impregnants (1.8-2.5% of the substance on the weight of graphite, or about 1/5 of the open pore volume) into anodes leads to virtually the same potential in each case. Impregnation with 100% linseed oil results in a greater increase of potential, especially if impregnation with linseed oil is not followed by chlorination. However, as the oil can separate out of the graphite pores during polarization [1], the potential is lower than would be expected if the pores were completely filled with the impregnating material.

The rise of potential of anodes impregnated with solutions of various substances is due mainly to displacement of the electrolyte to the surface, as was mentioned earlier in the discussion of data on the depth distribution of potential. Figure 4 shows that the curves for impregnated anodes in all the solutions are shifted to the left in relation to the curves for unimpregnated anodes by a value of about 0.3 for $\log D_a$. Thus, the behavior of impregnated anodes is similar to that of unimpregnated anodes, but at a doubled geometrical current density. According to the formula of Ksenzhek and Stender [9], at a given potential the geometrical current density is proportional to the square root of the specific surface of the electrode, and inversely proportional to the square root of the resistance of the electrolyte in the pores. As was mentioned earlier, the electrolyte resistance in the pores of an impregnated anode is approximately 3.5 times the resistance in an unimpregnated one. It follows that a twofold increase of the geometrical current density corresponds to a decrease of the specific surface of the graphite by a factor of 1.3. This estimate can hardly be regarded as strictly quantitative, because the equation of Ksenzhek and Stender was derived for a simplified model of a porous electrode. However, qualitatively it is clear that the increase of the true current density for impregnated graphite is due to both factors; the increase of electrolyte resistance has the greater influence.

Thus, the influence of the impregnant consists mainly of an alteration of the pore structure of the graphite. The nature of the impregnating substance appears to have virtually no effect on the anode process. This is indicated by the following facts. First, impregnation with 15% solutions of substances differing in nature results in approximately the same increase of potential in a given electrolyte. Second, the relative positions of the polarization curves for anodes with different impregnants are qualitatively the same in all solutions. Third, after introduction of impregnants into graphite, the slope of the polarization curves remains unchanged in all the electrolytes studied. Finally, as already mentioned, the shift of the polarization curves for different impregnants in different solutions is quantitatively the same ($\Delta \log D_a = 0.3$). Because of the different values of the coefficient b , equal shifts along the current-density axis led to different increases of potential. The quantitatively similar changes of the polarization curves for different electrode processes confirm once again that this influence is due not to the specific effects of impregnating substances on the electrode process but to geometrical changes in the pore structure of the graphite.

It is interesting to compare anode potentials in phosphoric and hydrochloric acid solutions at equal partial current densities for oxygen. The latter were found from the current efficiency for oxygen in electrolysis of dilute HCl (these data will be examined more fully in the next communication). Table 1 shows that the difference between the potentials in these solutions, at equal partial current densities with respect to oxygen, of impregnated and unimpregnated anodes does not exceed 0.02 V, i.e., it is within the limits of experimental error. Therefore, under conditions of approximately equal participation of chlorine and oxygen in the anode process, evolution of chlorine has no appreciable influence on the overpotential of oxygen liberation.

The observed changes in the course of polarization curves for acid solutions when a potential of 1.9-2.0 V is reached are probably due to changes in the structure of the surface graphite layers. It may be supposed that at 1.9-2.0 V a graphite oxide phase is formed; this leads to a sharp rise of overpotential, accompanied by intensified mechanical breakdown of the graphite anode [11]. It is significant that the change in the course of the polarization curves for acid solutions occurs at different current densities with different impregnants and for the unimpregnated anode, but at almost the same potential (1.9-2.0 V). In H_3PO_4 solution, for an anode impregnated with 100% linseed oil, this change already begins at 500 A/m².

CONCLUSIONS

1. Investigation of polarization characteristics of anodes impregnated with different substances, for evolution of chlorine and oxygen in different proportions, showed that 15% solutions of all the impregnants gave approximately the same increase of potential, corresponding to an approximately twofold increase of the geometrical current density for an unimpregnated anode.
2. The influence of impregnation on the electrode potential is due mainly to displacement of the electrolyte to the surface. This effect does not necessitate blockage of the internal pores, and is achieved by increase of the electrolyte resistance in the pores and, to a lesser extent, by shielding of the active surface.
3. The impregnants studied were not found to have any significant specific influence on the kinetics of chlorine and oxygen evolution.

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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.
