

INFLUENCE OF THE DEGREE OF PORE FILLING BY IMPREGNATION ON DURABILITY OF GRAPHITE ANODES*

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The purpose of impregnation of graphite electrodes used for chlorine production is to raise their durability by diminishing the destruction of graphite in the pores. It is known that if the pores are filled completely with the impregnating material the anodes are destroyed rapidly [1]. It is stated in certain patents that for effective protection the internal surface of the anode must be covered with a continuous polymerized film of the impregnating material [2-5]. Such impregnation does not essentially differ in any way from complete clogging of the pores, and should lead to intensified destruction of the graphite. Our investigations of the mechanism of protective action of impregnating materials partially filling the graphite pores showed that to obtain a significant effect it is not necessary to exclude completely the inner pores of graphite from electrolysis [6-8].

In this paper we report an investigation of the influence of the degree of pore filling with the impregnating material on the electrochemical durability of graphite anodes.

EXPERIMENTAL

The experiments were conducted on DÉZ graphite anodes (and in some cases NÉZ anodes) impregnated with various substances and with their solutions in a volatile solvent. When solutions were used, the graphite was impregnated completely with the solution and the solvent was then evaporated off. Ipatov's method [1] was

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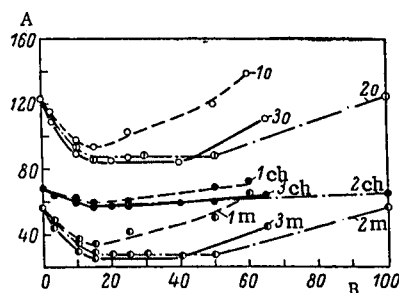


Fig. 1. Influence of the concentration of the impregnating material on wear of graphite anodes. A) Anode wear (g/100 A-h); B) concentration of impregnating material in solution (wt.%). Impregnating materials: 1) Etinol lacquer; 2) linseed oil; 3) tall oil; o) overall wear; ch) chemical wear; m) mechanical wear; the same in Figs. 2-4. Electrolyte - HCl of 5 g/liter concentration, 480 A/m², 70°; the same in Figs. 2-4

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TABLE 1. Potentials of Anodes Impregnated with Solutions of Tall Oil, Determined in Various Electrolytes at 1000 A/m² and 70°

Electrolyte	Anode potential (V) at concentration of impregnating material in solution (%)					
	0	10	15	30	40	45
Solution of HCl, 5 g/liter concentration	1.74	1.76	1.79	1.81	1.85	1.96
Solution of NaCl, 170 g/liter concentration (0.03 N HCl)	1.45	1.48	1.50	—	—	1.93
Solution of NaCl, 270 g/liter concentration (0.001 N HCl)	1.43	—	1.47	—	1.55	—

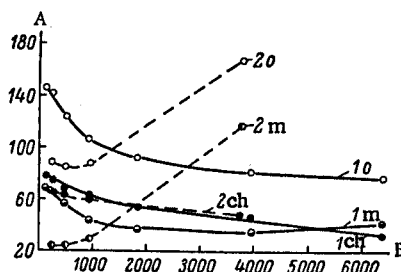


Fig. 2. Dependence of the wear of graphite anodes on current density. A) Anode wear (g/1000 A-h); B) current density (A/m²). 1) Unimpregnated graphite; 2) impregnated with 40% tall oil.

used for impregnation of the graphite specimens with 100% linseed oil. Impregnation of graphite with paraffin was performed as follows: various amounts of paraffin were removed from the impregnated specimens by heating at 250° for various times. The durability of impregnated graphite was determined by electrolysis of HCl solution of 5 g/liter concentration (accelerated method of testing anode wear) [7].

Our earlier investigation of the mechanism of action of impregnating materials incompletely filling the anode pores showed that their main role is to change the graphite structure favorably by covering the fine pores and regions of contact between the graphite grains with a film of material. Protection of the regions of grain contact against oxidation prevents premature crumbling of large grains, thereby greatly diminishing mechanical wear [8]. Accordingly, the effectiveness of impregnation must be determined to a considerable extent by the amount of impregnating material introduced into the anode, and consequently by the concentration of the impregnating solution.

It is seen from Fig. 1 that anode wear decreases rapidly with increasing concentrations of all the impregnating materials in solution from 0 to 15%. On further increase of concentration the wear either increases at once or remains at a roughly constant level in a certain concentration range and then rises sharply.

This course of the curves is explained as follows. On introduction of small amounts of the material (in impregnating solutions of up to 15% concentration), the material after removal of the solvent collects by capillary action mainly in fine pores and at points of grain contact. This results in increase of the true current density at the anode, which is accompanied by a small increase of potential.

As the result of impregnation with 15% solution (giving a weight gain of 2.0–2.5% of the impregnated anodes) the finest pores are excluded almost completely from action, and anode wear reaches its minimum value. On further increase of the solution concentration the nature of anode wear differs somewhat with different impregnating materials, because the distribution of the material in the pores varies in accordance with its physicochemical properties.

In the case of linseed and tall oils, with increase of the amount of substance up to a certain limit (of the order of 5% weight gain, impregnating solutions of up to 40–50% concentration) after filling the fine pores the substance begins to spread into larger pores. Because of the different surface–volume ratios of fine and

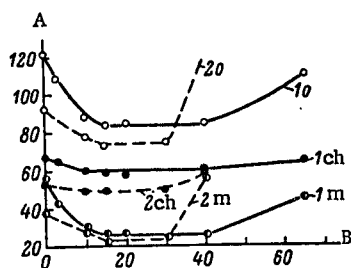


Fig. 3

Fig. 3. Influence of the concentration of the impregnating solution on the wear of graphite anodes at different current densities. A) Anode wear (g/1000 A-h); B) concentration of solution (tall oil) (wt.%). 1) At 480 A/m²; 2) at 2000 A/m².

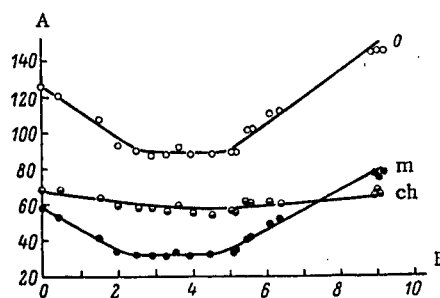


Fig. 4

Fig. 4. Influence of the content of impregnant in a graphite anode on its wear. A) Anode wear (g/1000 A-h); B) weight gain due to the impregnant (paraffin) (wt.%).

relatively large pores, a given amount of substance insulates a much smaller anode area in large than in fine pores. Therefore increase of the concentration of the impregnating solution within certain limits (15–50%) results in only a slight increase of the true current density and therefore of the potential, as is confirmed by the data in Table 1. The anode wear remains virtually unchanged.

In view of the fact that linseed oil is partially liberated from the anodes during electrolysis, the maximum permissible concentration of its solutions is somewhat higher than for tall oil. Finally, when an excess of impregnating material is introduced into the anode (from impregnating solutions of over 40–50% concentration) the material covers a larger proportion of the pore area. The true current density rises sharply and the anode potential increases to 1.9–2 V and higher; this is accompanied by intensified destruction of the anode, with stratification and nonuniform wear.

When the rapidly polymerizing Etinol lacquer is used for anode impregnation, increase of its concentration in solution above 15% leads to appreciable increase of anode wear. It can be inferred from certain indirect data (the relatively greater decrease of open-pore volume after impregnation, lower gas permeability) that the film which forms rapidly during drying of the lacquer covers the pores. Therefore even a comparatively small increase of the concentration of Etinol lacquer is accompanied by a substantial increase of current density and correspondingly of the potential. It should be noted that the intensified anode destruction resulting from the use of impregnating solutions of higher concentrations is due to a sharp increase of mechanical wear, while oxidation of graphite remains almost unchanged.

Analogous wear results were observed in hydrochloric acid solution at 1.9–2.0 V potential for unimpregnated anodes and anodes impregnated with 15% linseed oil solution [8]; this was attributed to formation of oxide phases, causing swelling of the graphite. Therefore potentials of 1.9–2.0 V are critical for graphite [6, 8]. Similar results were obtained by Éberil' and Filippov [9].

The adverse influence of the high true current densities corresponding to potentials above 1.9–2.0 V on the durability of graphite is confirmed by comparison of curves for the influence of current density on wear of an unimpregnated anode and an anode impregnated with 40% tall oil solution (the maximum permissible concentration). It is seen from Fig. 2 that at current densities in the range 250–1000 A/m² the wear of the impregnated anode is considerably less than that of the unimpregnated anode, while at current densities above 1000 A/m² it rises sharply owing to intensification of mechanical crumbling while chemical wear continues to decrease. In the case of the unimpregnated anode mechanical wear begins to increase only at current densities above 6000 A/m², when the potential is 1.9 V and more. Since the role of the impregnating agent reduces to mechanical coverage of part of the internal surface of the graphite and increase of the true current density, it is reasonable to expect that the limiting concentration of the impregnant must be lower for anodes used at higher current densities (Fig. 3). In fact, on increase of the current density from 480 to 2000 A/m² the lower concentration limit remains at 15% while the upper limit for the curve corresponding to the higher current density diminishes from 40 to 30%.

Intensified wear in presence of excess impregnant in the anode also occurs in other electrolytes. In an NaCl solution of 170 g/liter concentration an anode impregnated with 45% tall oil was destroyed completely

after only 20–40 h at 1000 A/m² current density. A rough calculation shows that with complete filling of the pores with the impregnant the rate of anode wear is higher than that of an unimpregnated anode by a factor of 15–20. According to literature data [10], anode wear in chloride–chlorate solutions also increases sharply in presence of excess impregnant. Therefore even if highly effective impregnating materials are used intensified destruction of anodes may occur if these materials are introduced in excess [1, 10–12].

Although the use of solutions of impregnating materials (with the exception of Etinol lacquer) of different concentrations in the range from 15 to 40–50% gives similar results with respect to anode durability, the preferred range for selection of the optimal concentration is 15–18%; in addition to economy of the impregnant, such solutions have some other advantages (somewhat lower potentials, lower solution viscosities, etc.).

We also determined the lower concentration limit for anodes of lower porosity (NÉZ type). Here again solutions of 15–18% concentration were found to be the best.

Experiments showed that the choice of the optimal concentration of the impregnating solution based on tests of anodes in electrolysis of dilute hydrochloric acid is equally valid for electrolysis of sodium chloride solutions. The lower limit of permissible concentrations, in our opinion, is determined by the amount of substance required to fill the fine pores in the graphite, and therefore is not related to the specific nature of the electrolyte.

The high effect of anode impregnation with 15% solutions of various substances in electrolysis of concentrated NaCl solutions is confirmed by both laboratory [8] and industrial tests.

When pure impregnants (not solutions) are used, the dependence of anode wear on the amount of substance remaining in the graphite after impregnation is the same as with the use of solutions (Figs. 1 and 4). The optimal residual content of the substance is the same in both cases. The protective action of the impregnant also remains the same; mechanical wear is diminished to a greater extent than chemical.

The optimal content of the impregnant in the anode depends to a considerable extent on the density of the graphite impregnated. The denser the graphite, the lower must the residual weight gain be. For example, the optimal contents of residual material in the pores of DÉZ graphite (density 1.69 g/cm³) and NÉZ graphite (density 1.57 g/cm³) are 2.0–2.5 and 4.0–4.5% on the graphite weight respectively. Sjodin and Wranglen [10] selected the optimum on the basis of a somewhat inapt comparison of specimens having different densities. Their value of 10% for the optimal weight gain is actually valid only for highly porous graphite. The graphite density is also disregarded in the optimal values given in certain patents [3, 4].

Impregnation with solutions is preferable to the use of pure substances, owing to its technological simplicity, easy imbibition of the solution by fine graphite pores because of its low viscosity, reduction of the consumption of impregnant by a substantial factor, and the possibility of introducing a previously polymerized substance into the anode pores. Moreover, it was found that when 15–18% solutions are used for impregnating graphite of any density introduction of the optimal amount of the substance into the graphite pores is achieved automatically, regardless of the density of the graphite, ensuring a high quality of impregnation. Control of the process merely involves ensuring complete removal of the solvent.

CONCLUSIONS

1. Correlation of the degree of filling of pores in graphite anodes with impregnants with the durability of anodes confirmed that inactivation of the finest graphite pores is a decisive factor for raising durability.
2. It was shown that the use of 15–18% solutions of impregnants in a volatile solvent is preferable for impregnation; the amount of substance introduced is determined by the porosity of the graphite.

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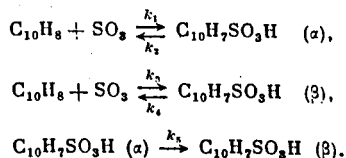
KINETIC PARAMETERS OF NAPHTHALENE SULFONATION IN DICHLOROETHANE AT LOW TEMPERATURES

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In earlier publications [1-3] we proposed a very simple model of naphthalene sulfonation by sulfuric anhydride in dichloroethane, with α -naphthalenesulfonic acid (α -NSA) as the end product. However, the calculation methods used gave only approximate values of the kinetic parameters of the process. The formulated model [2, 3] was insufficiently informative. It could be used for parametric investigations and for elucidation of the general relationships of the process. However, the values found earlier [3] for the kinetic coefficients are unsuitable for optimization of α -NSA synthesis, as they give good agreement between calculated and experimental concentrations only for corresponding temperatures.

In this paper we employ a somewhat different approach to determination of the kinetic parameters, ensuring adequate accuracy for practical calculations and optimization of the mathematical model of naphthalene sulfonation in dichloroethane in the temperature range 263-328°K. As stated earlier, sulfonation of naphthalene to the monosulfonic acid can be represented by the following scheme:



It was shown earlier [2, 4] that $\alpha \rightarrow \beta$ isomerization and hydrolysis of β -naphthalenesulfonic acid are virtually absent. Under the specified conditions, at 1:1 component ratio and 0.04-0.072 kmole/m³ concentrations of the original components, disulfo derivatives are not formed either [2].

At low temperatures, with stoichiometric amounts of the reactants and in absence of disulfonic acids in the reaction mass the process may be represented mathematically as follows:

$$\left. \begin{aligned} \frac{dC_1}{dt} &= k_1 C_3 C_4^0 - C_1 (k_2 + k_3), \\ \frac{dC_2}{dt} &= k_2 C_3 C_4^0 - k_4 C_2 + k_5 C_1, \\ C_3 &= C_3^0 - (C_1 + C_2), \\ C_4 &= C_4^0 - (C_1 + C_2), \end{aligned} \right\} \quad (1)$$

where C_1 , C_2 , C_3 , and C_4 are the concentrations of α - and β -naphthalenesulfonic acids, naphthalene, and sulfuric anhydride respectively; the zero superscripts refer to the corresponding concentrations at time $t = 0$; k_1 , k_2 ,

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