INVESTIGATION OF THE KINETICS OF THE ANODIC EVOLUTION OF CHLORINE ON NONPOROUS GRAPHITE

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The overvoltage of the liberation of chlorine on graphite coated with high-temperature pyrolytic carbon, and on graphite impregnated with melted polyethylene and melts of $PbCl_2$ and AgCl, was investigated. In all cases the existence of two portions of the polarization curves with slopes of 60-90 mV and 120-160 mV was detected. The stoichiometric number at the reaction on different types of anodes is from 1 to 1.7. The polarization capacitance is close to the double layer value. The combination of experimental data is well explained by decelerated barrierless discharging of chloride ions, which turns into normal discharging at increased current densities. The activation energy of barrierless discharging of chloride ions was determined, and the energy of the adsorption bond of chlorine to oxidized graphite (17 kcal and 22 kcal) was found from it. The preexponential factor for the discharging of chloride ions is close to that calculated according to the theory of absolute reaction rates.

This work is a continuation of our previous investigations of the kinetics of the liberation of chlorine on graphite [1, 2]. Polarization curves taken on porous graphite have two linear portions in semilogarithmic coordinates, with slopes of 120 mV and 240 mV; as it follows from the theory of the porous electrode [1, 3], they correspond to true values of the slopes of 60 mV and 120 mV, respectively.

This fact, in conjunction with data on the influence of Fe^{3+} and SO_4^{2-} ions on the kinetics of the liberation of chlorine, gave a basis for assuming the existence of barrierless discharging of chloride ions on graphite [2, 4]. This work presents new data pertaining to the liberation of chlorine on nonporous graphite.

METHODS

The cell for taking the polarization curves consisted of cathodic and anodic divisions, connected through a stopcock. The cathodic process, just as in [1], represented ionization of chlorine dissolved in the electrolyte. In addition to a graphite cathode, there was an auxiliary rotating graphite anode in the cathodic compartment, for preliminary electrolytic development of the solution. After development, chlorine was blown through the electrolyte into the anodic compartment. The cell was set up in an air thermostat, the temperature in which was maintained with an accuracy of ±0.3°C. The electrolytes were prepared in double-distilled water. The salts used were recrystallized twice and calcined. The experiments were conducted in electrolytes with the composition 1.5 M HCl + 2.5 M KCl. In certain cases neutral solutions of KCl were used.

High-temperature pyrocarbon, applied on a graphite substrate (for its properties, see [5]), as well as brand DÉZ graphite, in which the pores were filled with polyethylene, AgCl, or $PbCl_2$, were used as the nonporous electrodes. The porous graphite was impregnated with polyethylene at a temperature of about 300°C. In this case there was a partial decomposition of the polyethylene. The electrode was encased in a polyethylene band after impregnation. The end of the sample was ground and served as the working surface of the electrode. The porous graphite electrode was impregnated with lead chloride or silver chloride by anodic treatment in a melt of these salts at a current density of 0.5-1 A/cm^2. The side surface of the impregnated sample, as well as the current lead, were insulated by melted polyethylene, while the end was ground. For the rest, the experimental procedure was analogous to that described in [1]. The polarization curves on one sample were reproduced within 1-5 mV. The curves of the potential drop with time were taken with an S1-8A or S1-19A oscillograph. The differential capacitance was calculated according to the slope of the initial portion of the decay curve. The electric conductivity of the solutions was measured with an alternating current bridge.

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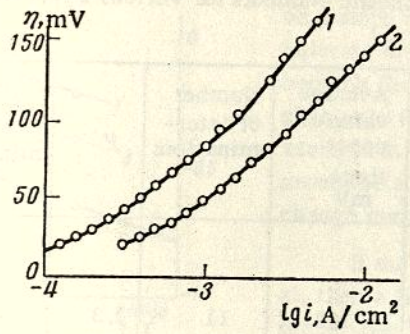

Fig. 1

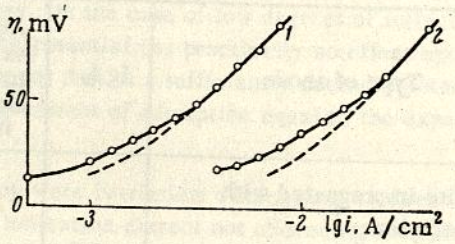

Fig. 2

Fig. 1. Influence of preliminary treatment of the surface of graphite impregnated with polyethylene on the overvoltage of the liberation of chlorine at 25°C, 1) after anodic oxidation in a weakly acid solution of KCl; 2) after cathodic reduction.

Fig. 2. Polarization curves obtained on porous graphite impregnated with: 1) $PbCl_2$; 2) AgCl. The dotted curves correspond to the mechanism of the usual decelerated discharging.

EXPERIMENTS AND DISCUSSION

For all types of graphite except for pyrocarbon, two linear portions with different slopes (Figs. 1 and 2) were detected on the polarization curves in semilogarithmic coordinates, taken in acid solutions. Anodic treatment in a neutral solution of KCl, to which electrodes of different types were subjected, with the exception of those impregnated with AgCl, in contrast to its influence upon the behavior of normal graphite, had practically no effect upon the shape of the polarization curves in an acid electrolyte. However, on the curves taken on pyrocarbon, two linear portions also became noticeable (Fig. 3). The polarization curves taken in neutral solution, just as on the usual graphite, lay far higher (by approximately 150 mV on pyrocarbon) than in acid solution (Fig. 3), which was due to a change in the state of the surface as a result of the liberation of oxygen simultaneously with chlorine [1, 2]. After cathodic treatment (the chlorine dissolved in the electrolyte was preliminarily removed by purging with nitrogen), to which the pyrocarbon and graphite impregnated with polyethylene were subjected, the overvoltage decreased, just as on normal graphite [1, 2] (Figs. 1, 3). The average values of the lower and upper slopes and logarithms of the exchange currents are presented in Table 1.

As can be seen from Table 1, the upper slope for all types of graphite is close to 120 mV (or somewhat higher). The lower slope is 60-90 mV (with the exception of unreduced pyrocarbon). In the case of impregnation with $PbCl_2$ melt, as we ascertained, the electrode obtained is entirely nonporous. In the case of impregnation with a polyethylene melt, the porosity of the electrode may reach several percent. The porosity of pyrocarbon is 1.8% [5]. Therefore it is probable that the somewhat increased slopes on pyrocarbon and graphite impregnated with polyethylene are due to the work of pores. In the region of the upper slope, the porosity was found to be low (especially on pyrocarbon), since at these current densities, as a result of the negligible porosity, there was a displacement of current onto the surface of the sample, and the electrode worked essentially as a nonporous electrode, but with a rough surface. On nonporous electrodes impregnated with molten salts, the lower slope practically coincides with the theoretical value 59 mV.

For all types of graphite we calculated the stoichiometric numbers from the formula $\nu = 2(i_0)_{extr}(d\eta/di)_{i\to 0}/(RT/F)$, where $(d\eta/di)_{i\to 0}$ was determined according to the slope of the linear portion of the curve. (In certain examples we also followed the linear portion in the direction of a more cathodic equilibrium potential—Fig. 4.) The average values of the stoichiometric numbers are also presented in the table. Despite the fact that the portion with slope 60 mV on graphite impregnated with $PbCl_2$ and AgCl is short, it is very pronounced. The fact that this portion is not the usual deviation from a semilogarithmic dependence when the equilibrium potential is approached was confirmed by the same method as in [2]. Actually, the polarization curves calculated according to the equation [6]

$$i = i_0\left[\exp\frac{\alpha'\eta F}{RT} - \exp\frac{(\alpha'-\lambda')\eta F}{RT}\right],$$

in which i_0, α', and λ' were selected so as to describe as accurately as possible the upper Tafel region, diverge substantially from the experimental curve in the region of low current densities (see dotted line in Fig. 2). The presence

TABLE 1. Average Values of the Logarithms of the Exchange Current Densities, Slopes, and Upper Portions of the Polarization Curves and Stoichiometric Numbers for Various Types of Graphite

Type of anode	lg i_0	Average value of lower slope, mV	Average value of upper slope, mV	Number of determinations	ν'	Number of determinations
Graphite impregnated with polyethylene:						
after oxidation	−4.9	80	163	11	1.3	5
after reduction	−4.4	82	138	11	1.3	5
Graphite impregnated with $PbCl_2$	−3.3	59	116	19	1.0	14
Graphite impregnated with AgCl	−2.6	61	119	8	0.95	3
Pyrocarbon after oxidation	−4.8	97	117	4	1.4	3
Pyrocarbon after reduction	−6.0	89	116	26	1.7	19

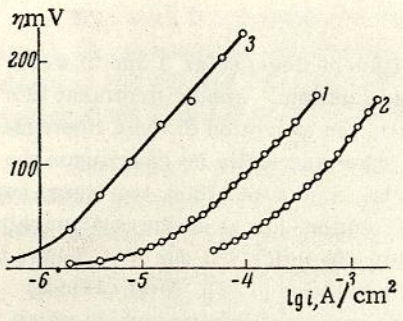

Fig. 3

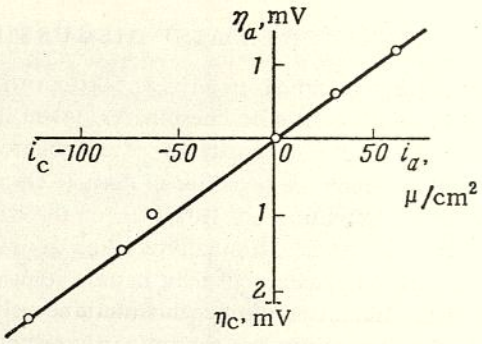

Fig. 4

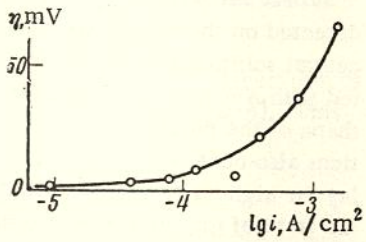

Fig. 5

Fig. 3. Influence of preliminary treatment of the surface of high-temperature pyrocarbon on the overvoltage of the liberation of chlorine at 25°C: 1) After anodic oxidation; 2) after cathodic reduction; 3) polarization curve in weakly acid KCl solution.

Fig. 4. Dependence of the overvoltage of the liberation of chlorine on the current density close to the equilibrium potential on graphite impregnated with $PbCl_2$. η_a) anodic overvoltage; η_k) cathodic overvoltage.

Fig. 5. Cathodic polarization curve on graphite impregnated with $PbCl_2$.

of two pronounced slopes, differing by two-fold, gives a basis for assuming the presence of barrierless discharging of chloride ions on the lower portion.

Generally speaking, various mechanisms may correspond to a stoichiometric number of one or two with a slope of 59 mV. Thus, at $\nu' = 1$, this is discharging, followed by electrochemical desorption (one of these two stages is slow and barrierless). At $\nu' = 2$, a barrierless adsorption-electrochemical mechanism [7-9], barrierless decelerated discharging with recombination removal, or decomposition of surface complexes containing one chlorine atom is possible. In addition, $\nu' = 2$ may correspond to a mechanism of discharging and electrochemical desorption at comparable exchange currents [6, 10].

In our experiments, similar kinetic functions were obtained regardless of the value of ν', which fluctuated from one to two. Therefore, it is most probable to assume that the determining step is barrierless decelerated discharging, followed by electrochemical desorption. Since a change in the state of the surface (various types of graphite) may affect the rates of these two steps to different degrees, the value of ν' may vary within the indicated limits, depending upon the ratio of their exchange currents.

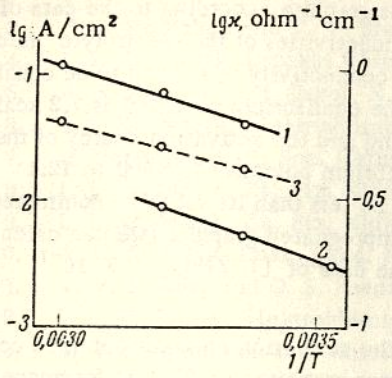

Fig. 6. Dependence of the logarith of the current density on 1/T for electrodes: 1) on porous graphite at η = 143 mV (calculated according to the data of [2]): 2) on graphite impregnated with $PbCl_2$, at η = 50 mV; 3) dotted line—dependence of the electric conductivity of a solution of 1.5 M HCl + 2.9 M NaCl upon 1/T.

If the slow step were discharging of surface complexes, then there could be a slope of 59 mV only at $\theta \ll 11$. In this case, in the ionization of chlorine the formation of these complexes (adsorption of chlorine) should become the slow step. In the case of low degrees of surface coverage, a change in θ with the potential has practically no effect upon the rate of adsorption. This means that at a sufficiently cathodic potential, there should be a limiting current of adsorption equal to the experimental exchange current.

If the slow step were barrierless discharging with recombination removal, then a limiting ionization current not exceeding the exchange current should also have been observed. Actually, to the degree to which the discharging of chloride ions is a barrierless process, the opposite reaction—ionization of chlorine—should not require activation. For an activationless process, the activation energy is equal to zero, and consequently, the ionization current should not depend upon the potential, if the rate of adsorption of chlorine is sufficiently great to maintain θ approximately constant. If adsorption cannot occur after ionization, then θ becomes less than the equilibrium value, and the limiting current will be less than the exchange current.

For analogous reasons, we can expect the limiting current in the case of rapid discharging, followed by slow barrierless electrochemical desorption, or in the case of an adsorption-electrochemical mechanism.

In the case of barrierless decelerated discharging, followed by the usual electrochemical desorption, however, the limiting current of the ionization of chlorine atoms will not be of the order of the anodic exchange current. Actually, with increasing cathodic potential, the rate of electrochemical adsorption will increase, which should lead to an increase in the concentration of adsorbed chlorine atoms. Therefore, the rate of ionization will increase despite the activationless character of the process. Thus, if the slow step in anodic polarization is barrierless discharging of chloride ions, then in the cathodic region the entire process is limited by the step of electrochemical adsorption.

In our experiments, close to the cathodic current equal to the exchange current for the anodic reaction, and even at higher current densities, there is no tendency for the appearance of a limiting current (Fig. 5). From this it also follows that the most probable mechanism of the evolution of chlorine is decelerated barrierless discharging, followed by the usual electrochemical desorption.

The low value of the differential capacitance, which we determined for a graphite surface impregnated with $PbCl_2$, is also evidence against the assumption of slow removal of adsorbed chlorine atoms. The average value of the capacitance (from nine determinations) is equal to 34 $\mu F/cm^2$, which is of the order of magnitude of the double layer capacitance and is evidence of an extremely small coverage of the surface by chlorine. A close value of the electrode capacitance was obtained on a porous graphite electrode in [11].

A lower degree of coverage means a low energy of adsorption of chlorine, which in our opinion is related to the degree of oxidation of the surface [2]. The decrease in the overvoltage after cathodic treatment, which we observed, just as in [1, 2], is evidence in support of this explanation. The low value of the capacitance, at the same time, indicates strength of the adsorption bond of the oxygen present on the graphite surface.

In [4, 12] it was shown that the real activation energy [13] for barrierless discharging at the equilibrium potential is equal to the heat of adsorption of the corresponding intermediate product. In view of this, we investigated the temperature dependence of the liberation of chlorine on graphite (Fig. 6).

The activation energies, calculated according to the formula

$$A = -R\left(\frac{\partial \ln i}{\partial 1/T}\right)_{\eta}$$

for two samples of graphite, impregnated with $PbCl_2$, at an overvoltage of 50 and 40 mV, proved to be between 6.1 and 6.3 kcal. From this, for the equilibrium potential, on the assumption that α = 1, the activation energy has a value of

7.2-7.3 kcal. This coincides with the activation energy calculated according to the extrapolated exchange currents. We also determined the activation energy of the discharging of Cl^- ions on porous graphite according to the data of [2] (Fig. 6). For this purpose, we preliminarily measured the specific electric conductivities of the electrolyte used in [2] (1.5 M HCl + 2.9 M NaCl) (Fig. 6). The activation energy of the electric conductivity was found to be equal to 2.33 kcal. The effective activation energy of the discharging of Cl^- ions at the equilibrium potential is 7.2 kcal. This value is an arithmetic mean between the true activation energy of discharging and the activation energy of the electric conductivity [14]. From this the true real activation energy at the equilibrium potential is equal to 12.1 kcal. Thus, the activation energy on graphite impregnated with $PbCl_2$ proved to be less than its value on nonimpregnated graphite, which agreees with the larger value of the exchange current on impregnated graphite (we can calculate the true exchange current density at 25°C for porous graphite according to the data of [1, 2]—$i_0 = 7.5 \cdot 10^{-7}$ A/cm^2).

Since the heat of formation of the chlorine atom is equal to 29 kcal [15], the activation energies obtained correspond to heats of cleavage of the adsorption bond of chlorine of 17 kcal for porous graphite and 22 kcal for nonporous graphite. This is less than what follows from the calorimetric data [16] for equilibrium coverage. This discrepancy is explained by the strong oxidation of the surface of the electrodes in our experiments. If the slow step were not discharging, but electrochemical desorption, then the activation energy of the process would have been equal to the heat of adsorption, taken with the opposite sign. Then the energy of the bond would have values of 41 kcal and 35 kcal for porous and impregnated graphite, respectively. These figures seem too large, if we consider the influence of adsorbed oxygen on the energy of the bond of chlorine. Moreover, as is shown by calculation according to the Temkin equation [17], such bond energies correspond to medium degrees of coverage of the surface, i. e., large values of the adsorption capacity, which contradicts the experimental data. At the same time, the energy of the bond, ~20 kcal, gives very low degrees of coverage of the surface, i. e., negligible adsorption capacity. The Temkin equation pertains to the Langmuir adsorption isotherm; at medium degrees of coverage, however, judging by the decrease in the heat of adsorption [16], a logarithmic isotherm is more probable. However, in this case the Temkin equation can give quantities with a correct order of magnitude, if the energy relating to the equilibrium degree of coverage is subsumed under the bond energy in it.

In [4, 12] a discrepancy (of three orders of magnitude) between the experimental and theoretical values of the preexponential factor was noted for the liberation of hydrogen on mercury. There also it was proposed that this discrepancy is most likely due to the approximations lying at the basis of the theory of absolute reaction rates. One of these assumptions is, for example, the assumption of a Maxwell-Boltzmann distribution of energy for the activated complexes. Since these approximations, generally speaking, are sensitive to the mass of the reacting particles, it may be assumed that for the discharging of the heavier chloride ion there will be a closer agreement of the theoretical and experimental values of the preexponential factor than in the case of hydrogen. The following equation was used to calculate the preexponential factor:

$$K = \varepsilon \frac{kT}{h} e\varkappa\, 10^{15}\, p_{Cl_2}^{1/2} (1 - \theta)\, e^{-1/2\, S^0_{Cl_2}/R}.$$

In its derivation, analogous to the derivation of the corresponding equation for the discharging of hydrogen ions in [4, 12], we considered the fact that in the barrierless process the activated state coincides with the final state, and consequently, the entropy of the activated complex should be equal to the entropy of the activated chlorine atom. The preexponential factor calculated according to this equation proved equal to $10^{3.5}$ A/cm^2. The experimental values found for the liberation of chlorine on normal graphite and on graphite impregnated with $PbCl_2$ are equal to $10^{2.8}$ A/cm^2 and 10^2 A/cm^2, respectively. The calculation of the preexponential factor for porous graphite required a transition from apparent current densities to true current densities according to the equations of the theory of the porous electrode [1, 3]. In this case we used the following parameters: the specific surface of graphite was equal to 2 m^2/cm^3, and the ratio of the specific electric conductivity of the electrolyte in the volume to the electric conductivity in the pores was equal to 46 [11, 18]. From a comparison of the values cited above it is evident that far better agreement of the experimental and theoretical values is observed for the discharging of chloride ions. Thus, actually the discharging of a heavy ion is considerably better described by the equations of the theory of absolute reaction rates.

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