ELECTROCHEMICAL OXIDATION OF A GRAPHITE ANODE

I. POLARIZATION BEHAVIOR OF THE ANODE AS A FUNCTION OF SOLUTION COMPOSITION AND TEMPERATURE

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There is a large number of papers dealing with studies of the destruction of graphite anodes during the industrial manufacture of chlorine and chlorates. It is a universally accepted viewpoint that the destruction of graphite during electrolysis is due to its oxidation by oxygen being first evolved at the anode [1].

The electrochemical oxidation of graphite in the absence of chloride discharge was studied in [2-4] at potentials below the oxygen equilibrium potential, in [5-12] at higher potentials approaching the conditions of industrial electrolysis. Tafel dependences with slopes of 150-180 mV were found; these slopes increase in the region of 1.9-2.0 V, and this is accompanied by a sharp intensification of the wear [6,9,10].

The most detailed study of anode potential as a function of pH is available in [11], but only over a very narrow range of current densities. The influence of anions such as sulfate, which intensify the wear of the anodes in chlorine electrolysis, has been studied in [7, 13-19]. However, the availability of data which would characterize the oxidation of graphite over a wide range of electrolysis parameters (potential, pH, temperature, solution composition) is extremely limited so far. We have set ourselves the task to obtain such data.

Polarization curves were recorded for porous graphite and for graphite impregnated with polyethylene, in phosphate solutions at two values of ionic strength and over a wide range of pH (0.4-14), temperatures (20-80°C), and current densities (10^{-5}-$3 \cdot 10^{-2}$ A/cm^2); experiments were also run with the addition of various sulfate concentrations. The electrodes were sheets measuring 20 × 27 × 1 mm which were cut from DEZ graphite having a porosity of about 20%; their apparent surface area was approximately 11 cm^2. The electrodes were cleaned by boiling in 6 N HCl and then washed free from the HCl by boiling in distilled water and drying at 110-120°C. Impregnation of the graphite with polyethylene was done by immersing an electrode heated to 250°C for 8-10 min into molten polyethylene. The salts were twice recrystallized, the H_3PO_4 was purified by freezing out twice, the H_2SO_4 was purified by distilling twice. The solutions were in addition purified by electrolysis at Pt electrodes. Stationary polarization curves were recorded in the usual way under galvanostatic conditions. Purified nitrogen was passed through the cell with separate cathode and anode compartments during the experiment. The potentials are reported with respect to the normal hydrogen electrode.

The following technique of recording the polarization curves was used to obtain reproducible results. Each series of experiments was performed on one electrode. A new electrode, for its preparation, was always placed into an H_3PO_4 solution (1 M), and for several hours polarized anodically with a current density of about 10 mA/cm^2 until it had reached a constant potential. Stationary polarization curves were then recorded in solutions of various pH. When the series was completed, a control experiment was run under the conditions of the first experiment. The difference between the data of the first and the control experiment was no greater than 15 mV.

The polarization curves for porous graphite over a pH range of 0.85-14 are shown in Fig. 1. In acidic solutions at potentials above 1.55 V the slope b = 150-170 mV, but below 1.55 V it is larger than

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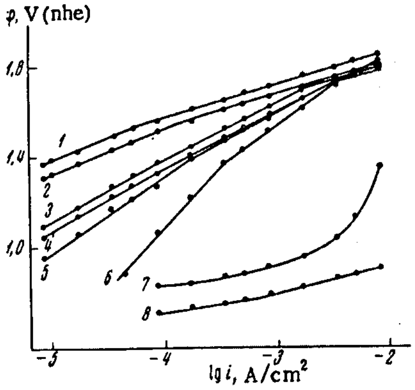

Fig. 1

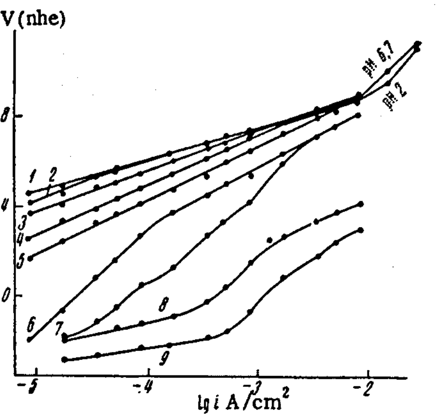

Fig. 2

Fig. 1. Polarization curves, φ against log i, on a porous graphite anode in phosphate solutions (ionic strength of the solutions: 0.14). Temperature: 20°C. Solution pH: 1) 0.85; 2) 2.0, and 3.4; 3) 6.9; 4) 7.9; 5) 10.0; 6) 11.7; 7) 13.0; 8) 14.0. The solutions for pH 13 and 14 were KOH without phosphate.

Fig. 2. Polarization curves, φ against log i, at a polyethylene-impregnated graphite electrode in phosphate solutions (ionic strength of the solutions: 0.14). Temperature: 20°C. Solution pH: 1) 0.84; 2) 2.0; 3) 4.0; 4) 6.4; 5) 7.7; 6) 10.0; 7) 11.8; 8) 13 (the solution: 0.1 M KOH + 0.035 M K_3PO_4); 9) 14 (the solution: 1 N KOH + 0.035 M K_3PO_4).

200 mV. The curves are steeper in neutral and weakly alkaline solutions. In the pH range 0.85-12 the polarization curves approach one another at about 1.8 V. In alkaline solutions the potential drops very strongly, and the slope decreases to 70 mV. The reproducibility of the curves in strongly alkaline solutions is somewhat inferior.

Polarization curves for the impregnated electrode are shown in Fig. 2. The general character of the pH dependence of potential is the same for the two types of electrode. However, on the porous electrode the potential is always lower (e. g., at pH 0.85 this difference is about 80 mV), and the slope b is always higher (by a factor of 1.2 to 1.3), then that on the impregnated electrode. In strongly acidic solutions (pH 0.85-2.0) the potential is pH independent over the entire range of current densities on the impregnated electrode. In alkaline solutions (pH 13 and 14) one also observes a section with low slope ($b \simeq 70$ mV), but at higher potentials the slope rises sharply (to 300 mV), and decreases again somewhat when the current density increases further. At polarizations above 1.9-2.0 V an increase in the slope is observed on the polarization curves both in acidic (pH 2) and in neutral (pH 6 and 7) solutions.

In acidic solution at pH of about 1, the polarization curves are shifted towards lower potentials when Na_2SO_4 (0.22-1.0 M) is added to 0.1 M H_2SO_4. Increasing the ionic strength of the buffer from 0.14 to 0.4 has a similar effect; the decrease in potential is more pronounced at lower potentials (below 1.5 V). In alkaline solutions, to the contrary, increasing the ionic strength of the solution leads to a shift of the polarization curves toward higher potentials. Sulfate seems to be strongly retained by the electrode, because the initial curve cannot be reproduced when its concentration subsequently is decreased.

The pH independence of potential in strongly acidic solutions and the decrease in potential when increasing the ionic strength of the solution make it appear likely that oxygen is evolved via the discharge of water molecules. The strong pH dependence of potential at high pH and the inhibition of the reaction in this region by sulfate addition point to an electrochemical reaction involving the OH^- ion.

It follows from polarization measurements performed at room temperature that the true working surface area of porous graphite in the stationary state, e. g., at a current density of about 10 mA/cm², is increased by a factor of about 50 as compared to a new anode (the potential decreases by 230 mV while the slope of the polarization curve is 150 mV). The true working surface area of the impregnated anode in the stationary state is three to four times smaller than that of a nonimpregnated anode. During preliminary treatment this area increased by a factor of 15 to 30. Taking into account that the roughness factor of mechanically treated graphite will hardly be lower than two we find that in the stationary state, impregnated graphite had a roughness factor of 30-60 or more.

The porous anode used in our experiments had a working thickness of 0.5 mm, which is appreciably less than the depth to which the process will penetrate, i.e., several millimeters for the evolution of oxygen [3]. One can expect, therefore, that the distribution of current and potential over the depth of the electrode must be nearly even. The value of b found experimentally for the porous electrode is 1.2 to 1.3 times higher than that for the impregnated electrode, i.e., the distribution of current and potential still was not quite uniform, although it was nearly so. It is possible that some of the nonuniformity was due to an accumulation of acid in the depth of the anode, viz., to pH 2 when the pH in the bulk of the anolyte was 4 (this was determined by the technique of [20]).

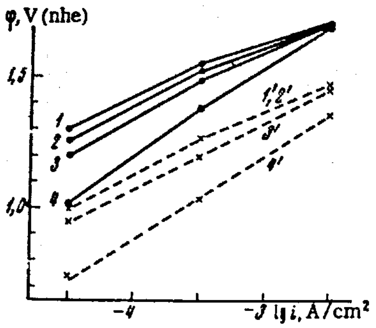

Fig. 3. Polarization curves, φ against log i, at a porous graphite anode in phosphate solutions (ionic strength of the solutions: 0.14) at 40°C (solid lines 1-4) and at 80°C (dotted lines 1'-4'). Solution pH: 1) 0.85; 2) 2.5; 3) 4.5; 4) 6.9.

In acid solutions the agreement between the data obtained by us and those of the literature is quite satisfactory. For example, on pyrographite [5] and on the impregnated graphite the b values are the same, about 150 mV; the surface area of our impregnated electrode was 15-25 times larger than that of pyrocarbon (for an estimate of the latter's surface area see [5]), which corresponds to a difference of 180-210 mV in overpotential, i.e., close to the observed $\Delta\eta$ = 270 mV. A certain difference in overpotential can be due to the greater regularity of the structure of pyrographite. Our data for porous graphite (taking into account the temperature coefficient) are 30-60 mV above those of [6, 7, 11], but this is due to the fact that in our case the electrode was very thin, and its true working surface area was less than that of the thick electrode in [6, 7, 11]. The disagreement becomes somewhat higher when going to higher pH. Thus, in [11] there is a continuous decrease in potential between pH 1 and pH 7 totalling 180 mV while in our work the potential is practically constant. However, in our experiments the ionic strength of the solution remained constant (0.14), while in [11] it rose from 0.1 to 3.0. In this pH range we have observed a decrease in potential by 30-100 mV when raising the ionic strength from 0.14 to 0.40. It seems, therefore, that the effect observed in [11] should to a larger extent be attributed to the change in ionic strength than to any change in pH.

Besides room temperature we have also studied the oxidation of graphite, impregnated as well as porous, at elevated temperatures (40, 60, and 80°C); in these experiments the graphite anode and the calomel reference electrode were at the same temperature (in Fig. 3, the data are shown for a porous electrode at temperatures of 40 and 80°C). The energy of activation of the electrode reaction was determined from the temperature dependence of reaction rate.* The potential dependence of the energy of activation at various pH is shown in Fig. 4; the slopes of these relations yield the transfer coefficient α. The values for this are: α = 0.41 (0.33) at pH 0.85; α = 0.35 (0.33) at pH 2.5; α = 0.37 (0.28) at pH 4.5; and α = 0.25 (0.26) at pH 6.9. The α values obtained from the slopes of the polarization curves are indicated in parentheses. Considering the great sensitivity toward experimental error when determining the energy of activation one should acknowledge that the agreement between these α values is satisfactory. This, together with the common shape of the polarization curves at various temperatures, indicates that the mechanism

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* Plots of log i against 1/T were constructed at various pH and constant potential as referred to the reversible hydrogen electrode in the same solution, rather than constant overpotential [21], because owing to the complex and moreover changing composition of the anodic products it is difficult to select any one electrode reaction to which the equilibrium potential would have to be referred. This affects the absolute value of the energy of activation; hence, one must not compare energies of activation at different pH. However, the correction for another reference electrode has no effect on the potential dependence of the energy of activation; therefore, the α values at different pH can be compared.

of the process probably does not change with temperature. Comparison of the polarization parameters with the surface state of the anode and the composition of the anodic products will be reported in the following communication.

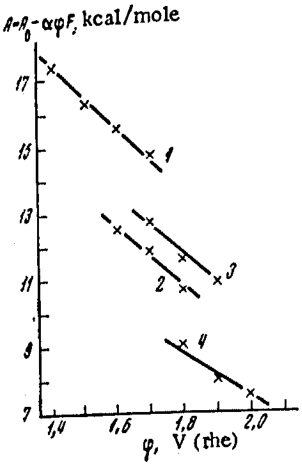

Fig. 4. Potential dependence of the energy of activation of the anodic process on porous graphite in phosphate solutions. The solution pH is the same as in Fig. 3.

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