ELECTROCHEMICAL OXIDATION OF THE GRAPHITE ANODE

III. COMPOSITION OF THE ANODIC PRODUCTS AS A FUNCTION OF THE SURFACE STATE OF THE ANODE AND OF ITS POLARIZATION CHARACTERISTICS

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The gas composition during the anodic polarization of graphite in the absence of chloride has been studied in a number of works (see, i.e., [1]), including, in recent years, [2, 3]; it was especially fully studied in [4]. According to the data of [4], the current yield (c. y.) of CO_2 is 91%, that of O_2 is 3%, and that of CO is 6% at pH between 1 and 6.7. When the pH is raised from 6.7 to 13, the c. y. of O_2 rapidly rises (from 3 to 95%), that of CO_2 strongly falls (to 5%), and CO almost disappears. In strongly alkaline solutions (pH 13 and 14), the gas composition remains almost unchanged, and the c.y. of O_2 is 95%. However, these results were obtained over a very narrow range of current densities, so that one cannot extend them to a wider range of conditions.

We have determined the composition of the anodic gases and the c.y. of CO_2 and O_2 at polyethylene-impregnated graphite under the same conditions where polarization curves and charging curves had been recorded [5, 6]. As in the preceding work, a new electrode was at first treated in 1 M H_3PO_4 until it had reached a stationary state (with respect to potential and with respect to the evolution rate and composition of gas). The experiments were run from higher to lower potentials. The anode was placed under the buret funnel, and the rate of gas evolution from the anode was determined; the current yields were determined from the composition of the mixture. The balance added up to ±2%. In acidic and neutral solutions all three constituents of the gas mixture were determined, but in alkaline solutions only O_2 and CO, while CO_2

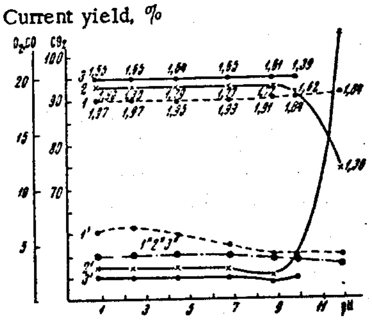

Fig. 1

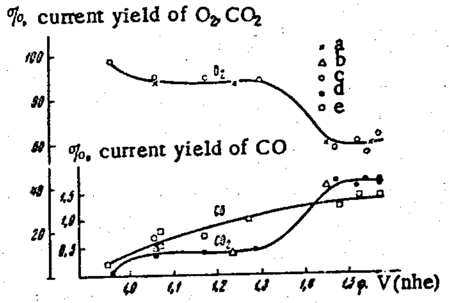

Fig. 2

Fig. 1. Current yields of CO_2 (1-3), O_2 (1'-3'), and CO (1"-3") as functions of solution pH at i values of: 1) 9.2, 2) 1, and 3) 0.12 mA/cm^2. Temperature 20°C. The values of potential (vs nhe) are indicated near the corresponding points.

Fig. 2. Current yields of CO_2 (b and d), O_2 (a and c), and CO (e) as functions of potential in solutions with pH 13 (a and b), pH 14 (c and d), and pH 13 and 14 (e).

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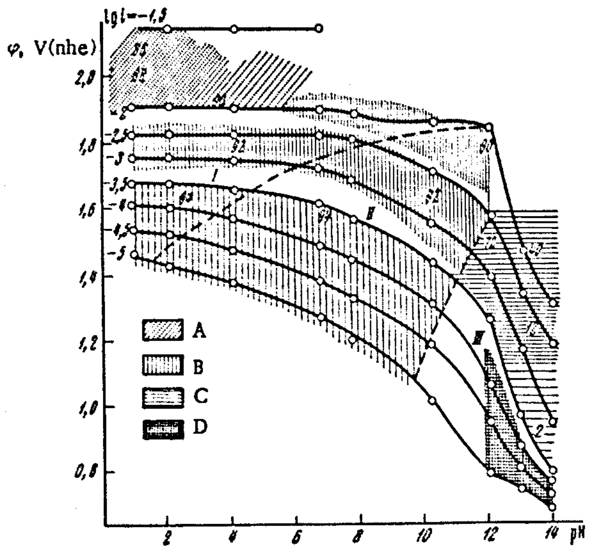

Fig. 3. The pH dependence of the potential of an impregnated electrode at constant current density (the log i are indicated at the curves). Temperature 20°C. Three typical regions, I, II, and III, which are explained in the text, are marked out in the figure; also marked out are the regions where different types of oxygen film exist, which correspond: A) to a plateau on the cathodic charging curves at 1.58 V (rhe); B) to the absence of a plateau on the charging curves; C) to a plateau on the cathodic charging curves at ~ 1.3 V (rhe); and D) to the absence of a plateau on the charging curves and to a more reversible type of oxygen adsorption. A change in the density of the hatching is a qualitative indication of a change in the amount of oxygen on the surface. The figures indicate CO_2 c.y. (in %).

was determined by difference. The composition of the gas mixture was determined in a gas microburet where the gas volume was measured and the gas treated with a chemical absorbent [7] in the same chamber.

The chief results on the pH dependence of CO_2 and O_2 c.y. are shown in Fig. 1. It can be seen that in harmony with the literature data, the anode gas consists mainly of CO_2 at pH between 0.85 and 10. The CO_2 c.y. is almost pH independent, but it increases somewhat (from 90 to 95%) when the anodic potentials are decreased. The CO c.y., which is about 4%, is practically independent of potential and pH. The O_2 c.y. increases somewhat with potential; it does so more rapidly above 1.9 V (up to 12% at pH = 0.85 and $\varphi \sim 2.1$ V).

It can be seen from Fig. 2 that in strongly alkaline solutions (pH 13 and 14), oxygen is the chief product of the anodic reaction at potentials up to 1.3-1.4 V (nhe); when the potential is raised to higher values the O_2 c.y. drops to 60%, and the CO_2 c.y. increases from 2 to 40%. CO_2 c.y.'s of such a magnitude have not previously been described in the literature for alkaline solutions. In this region the O_2 c.y. is practically pH independent. The product composition at pH 12 is found to be intermediate between the behaviors of graphite in acidic and in strongly alkaline solutions. It is interesting to compare the polarization behavior [5], the character of the anodic surface film [6], and the composition of the anodic products being formed over a wide range of pH and potentials. Figure 3 shows φ-pH curves at constant log i according to data from [5] for impregnated graphite. These curves have three typical regions.

The first region (denoted by I) is characterized by pH independence of potential. A decrease in electrode potential with increasing ionic strength of the solution, pH independence of the yields of the anodic products, and always the same type of oxygen surface film (no plateaus on the charging curves) distinguish this region. In Fig. 3 this type of surface film is denoted by vertical hatching; increasing density of the hatching corresponds to a larger oxygen concentration on the surface. Taken together all these data indicate that in this range of pH and potentials, one primary electrode process always occurs most likely as the slow step, or one of the slow steps of the reaction, viz., the discharge of water molecules. Above 1.9 V, even though the potential remains pH independent, the type of surface film changes; plateaus appear on the cathodic charging curves (diagonal hatching in Fig. 3). The change in the surface state of the anode causes the O_2 c.y. to increase by a factor of 2 to 3, and there is a sharp increase in the crumbling of the graphite. The appearance of plateaus on the charging curves is also accompanied by a sharp increase in the slope of the polarization curves (from 170 to 300 mV; see Fig. 2 in [5]).

The second region in the φ-pH dependence is characterized by substantial though not very strong pH dependence of potential. The φ-pH curves have a slope which increases with decreasing potential and with increasing pH. In this region, the electrode process is of a more complicated nature, because OH^- ion discharge seems to occur besides H_2O discharge. The type of surface film remains the same as in the first region, but as mentioned in [6], quantitative superposition of the charging curves at different pH is not observed to occur at identical potentials in this second region, in contrast to the first region. In Fig. 3, regions of coinciding charging curves are marked out by like density of vertical hatching; from it one can see that such coincidence is observed at identical current densities, i.e., the reaction rate turns out to be directly connected with the quantitative features of oxygen adsorption. This may imply that some step following the discharge of H_2O or OH^- plays an essential part in the overall mechanism of the process.

In the third region, which covers alkaline solutions, one observes a strong pH dependence of φ; there is a sharp change of φ when one goes from pH 12 to pH 13 (up to 400 mV), while the potential falls by 100-110 mV/pH unit in the region between pH 13 and pH 14. Increasing the ionic strength (adding sulfate) in strongly alkaline solutions leads to an increase in potential. Taken together the experimental data let it appear likely that OH^- ion discharge is the chief electrode process in the pH range 13-14. At low potentials (up to 1.6 V vs rhe) the charging curves lack plateaus (cross-hatched in Fig. 3). In this region the polarization curves have a low slope (60-80 mV), and the O_2 c.y. is 97%. We note that the charging curves in this region are relatively close to reversible curves, so that one can link the low "b" value to the existence of an equilibrium of the type $OH^- \rightleftharpoons OH_{ads} + e$ on the electrode. A plateau appears at higher potential on the charging curves, i.e., the surface state changes (horizontal hatching). The change in surface state is accompanied by a sharp increase in the slope of the polarization curves, up to 300 mV (Fig. 2) [5]. The amount of oxygen adsorbed increases with potential up to 2.1-2.2 V (rhe), and then it decreases At this potential one observes a decrease in the slope of the polarization curves to about 200 mV, and a sharp increase in the CO_2 c.y. (to 40%). In all probability the OH^- ion is the discharging particle here. It is hardly correct to assume, therefore, as done in [4, 8], that the ratio of the current yields of O_2 and CO_2 will characterize the contributions of H_2O and OH^- discharge to the overall reaction.

The electrode behavior at pH 12 is of an intermediate nature: at low potentials it is similar in type to region III, and at high potentials it is similar to region II.

Thus, the intimate connection between the kinetic parameters (the shapes of the $\varphi-\log i$ curves, the $\varphi-$pH dependence, and the correlation of the final reaction products with the surface state of the electrode) is a characteristic feature of graphite oxidation and oxygen evolution. Every change in the type of oxygen film is clearly manifest in the substantial variation of all other process parameters.

As noted in [6], the cathodic and anodic charging curves as a rule do not coincide. There exist on the surface appreciable amounts of oxygen (depending noticeably on potential) which are in a state of nonequilibrium adsorption; this shows that oxygen is removed sufficiently slowly from the surface. The complex nature of the change in oxygen film with pH and potential compels us to suggest that at least under certain conditions more than a single step is slow in the process. The marked effect of ionic strength of the solution shows that in acidic as well as in strongly alkaline solutions, one of the slow steps is of an electrochemical nature.

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