BRIEF COMMUNICATIONS

ANODE OXIDATION KINETICS OF GRAPHITE

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The authors have studied the electrochemical oxidation of graphite by plotting polarization curves. A spatula-shaped electrode of DÉÉ graphite (1.5 x 1.5 x 0.5 cm) was screwed into a Teflon collar, fixed tightly on a glass tube, and sealed in the lid of a Ж-shaped cell. The electrode was pressed tightly against a bottom-fed electrolytic switch. The anode contacts for the current and potential leads were two tantalum wires running through small holes in the glass. The electrode was polarized on both sides, both cathodes being separated from the anode space by flooding taps and Schott filters. Before an experiment the graphite electrodes were boiled continuously in pure HCl (replaced by fresh acid at intervals) until the solution was colorless, and then boiled in bidistillate.

Phosphoric acid of C.P. grade was purified by freezing twice. Sodium sulfate was recrystallized from bidistillate and dried. NaOH was obtained by decomposing sodium amalgam in bidistillate; in some experiments we used solid alkali of C. P. grade, thoroughly washed with bidistillate. Perchloric and sulfuric acid of C. P. grade were used without further purification. All the solutions were prepared from twice distilled water. Immediately before an experiment the solution was subjected to additional electrochemical purification in a separate apparatus. The use of an anode with a large surface ensured high efficiency. Reproducible results were obtained after a period of 2 h.

The potential was measured with a PPTV-1 potentiometer, the current strength with an M-104 ammeter. The curve was determined from high current densities to low densities, and vice versa. The electrode was retained at each current density until the potential was constant for 20-40 min. In the first 2 to 3 days of continuous electrolysis the potential fell (owing to increase in porosity and some surface development of the electrode) and then became stable. All the polarization curves relate to the steady state—they remained virtually unchanged after a day's continuous electrolysis.

The small thickness of the anode ensured relatively uniform current distribution over the whole depth of the electrode. The current-distribution character was assessable from approximate equations in [1]. It was found that for the most uniform distribution conditions—the highest current density in the least conducting solution— the true current density on the anode surface was about 6 times greater than at the center. At lower over-all current densities in the range corresponding to the major part of the polarization curve area studied, the difference between the maximum and minimum true current densities varied from a few percent to more than 20%, i.e., there were grounds for assuming that the electrode operated practically uniformly over the whole depth*. Here and below we shall therefore consider the potential versus the current density per unit volume of electrode (which is proportional to the true current density).

Figure 1 gives polarization curves obtained in phosphoric acid and in phosphate buffers (overall PO_4^{-3} concentration 3 g-ions/liter). The curves display close agreement of the semilogarithmic relation with slope b = 160-180 mV. At higher temperatures (25-60°) the curve shape is retained, except in the upper part (pH 3) where there is a fairly marked, but not reproducible, upward deviation. In this solution the activation energy at potential 1.3 V with respect to a hydrogen electrode is ~15 kcal.

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*The estimate of the nonuniformity is evidently too high, because it is difficult to assess the fall in electrolyte resistance in the anode pores, related to expansion and straightening of the pores due to steady oxidation of the graphite. The fact that in phosphoric acid the curves remain linear up to the highest current densities studied indicates that in fact the current distribution nonuniformity over the depth is much less than the above assessment.

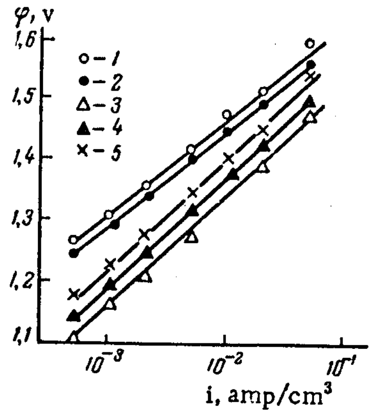

Fig. 1. Polarization curves in phosphate solutions: 1) pH 1; 2) the same + 0.2 M Na_2SO_4; 3) pH 3; 4) the same + 0.2 M Na_2SO_4; 5) pH 2.

Close values of b were also obtained in solutions with different pH with base electrolyte 5 M or 3 M perchlorate and 1.5 M or 2 M sulfate. Figure 2 plots potential versus pH in different solutions.* In all the solutions, at a certain pH the electrode potential (with respect to a normal hydrogen comparison electrode) fell by 0.06 V per pH unit with increasing pH (in perchlorate solution the fall may be sharper in the initial stage). At lower pH, in sulfate and, particularly, in perchlorate solutions the relation between potential and pH is absent. A roughly similar picture was obtained in [2] for anodes of pyrolytic carbon.

Gas analyses by a method very similar to that in [3] showed that the main electrolysis product was CO_2. The contents of CO and O_2 were ten times smaller. These facts are best explained by supposing that there occurs slow decomposition of the surface oxides (in the range with $\partial\varphi/\partial pH = 0.06$ V) or slow electrochemical desorption of CO_2 during discharge of H_2O molecules ($\partial\varphi/\partial pH = 0$). However, it should not be forgotten that the anode oxidation mechanism of graphite is greatly complicated by complex adsorption phenomena, which may be combined with penetration of ions and molecules between the planes of the graphite lattice [4]. These complicating factors are indicated, for example, by the opposing effects of sulfate at pH 1 and 3 in phosphate solutions (cf. Fig. 1); again, in several cases we observed that the composition of the solution in which the anode was pretreated had an effect on the anode potential in the solution; furthermore, the potential in 5 M ClO_4^- was approximately 80 mV higher than in 3 M ClO_4^- (at constant acidity), etc. Adsorption and introduction of anions evidently have a marked effect on the reactivity of surface oxides. Other stages of the process may also have an effect.

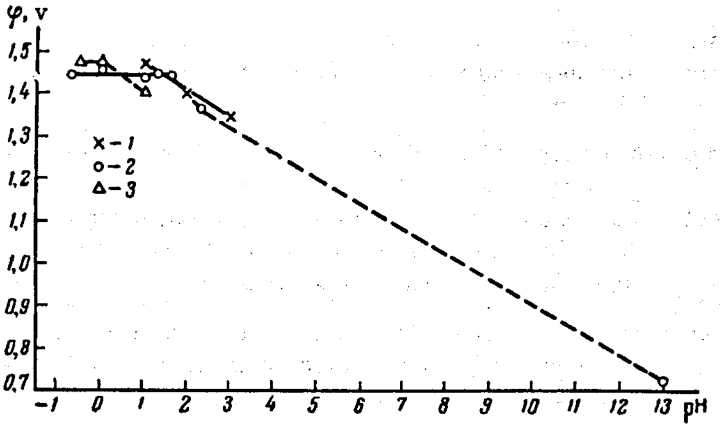

Fig. 2. Potential with $i = 10^{-2}$ amp/cm³ versus pH: 1) 3 M PO_4^{-3}; 2) 5 M ClO_4^-, 3) 1.5 M SO_4^{-2}.

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* The data relate to anodes pretreated to constant potential in a solution with the lowest pH of the solutions with the given anion. Each point is the mean of several determinations.