KINETICS OF OXYGEN GENERATION ON GRAPHITE AT LOW ANODE POTENTIALS

(UDC 541.13)

N. G. Bardina and L. I. Krishtalik

Institute of Electrochemistry, USSR Academy of Sciences, Moscow

Translated from Élektrokhimiya, Vol. 2, No. 2,
pp. 216-221, February, 1966
Original article submitted May 18, 1965

We plotted polarization curves on pyrolytic carbon in phosphate and chloride solutions with different pH in the potential region 0.4-1.2 V (sat. o. eL), i.e., lower than the equilibrium oxygen potential. In this potential region we observe linear dependence of the current on the potential. At the given current density the electrode potential is virtually independent of the pH. The assumption is made that in the region where the current is linearly dependent on potential, the oxygen is removed from the graphite surface in the form of CO_2 through barrier-free electrochemical desorption.

The anode processes of technical electrolysis are accompanied by the generation of oxygen both in the form of free O_2 as well as oxides forming on the electrodes.

In the case of a graphite anode the generation of oxygen is particularly harmful since it oxidizes the graphite into carbon dioxide, thereby causing destruction of the anode [1].

Data available on the oxygen discharge on graphite relate basically to the joint generation of oxygen and chlorine, and the studies were carried out with porous material, which has caused further complications. Earlier papers dealing with the generation of oxygen on graphite unfortunately do not give any idea of the mechanism of oxygen generation [2, 3]. We considered it of interest to study the kinetics of oxygen generation on nonporous graphite of a compact structure and, unlike papers submitted earlier, to study as well the potential region that is below the oxygen generation potential.

As material for the anode we selected high temperature pyrolitic carbon. The thickness of the virtually nonporous coating was 1.5 mm and the specific resistance of the pyrolytic deposit, measured along the plane of the graphite grid was $1.1 \cdot 10^{-4}$ ohm·cm, and in a perpendicular direction 3 ohm·cm.* According to published data [4, 5], deposits obtained in this way consist of graphite scales, the axis of which is normal to the surface of the graphite rod. The density of the deposit is 2.1 g/cm^3, and its x-ray density is 2.22 g/cm^3, i.e., close to the theoretical value of 2.265 g/cm^3. This is an indication of the great compactness of the pyrocarbon structure.

EXPERIMENTAL PART

The polarization curves were plotted in a cell with the anode and cathode space divided by taps. A pyrocarbon graphite rod 1.2 cm in diameter pressed into teflon served as the anode. The current lead made of copper wire had a slotted end by means of which it was screwed to the graphite. In view of the fact that the resistance of pyrolitic carbon is anisotropic, high ohmic losses might have been feared. But the resistance of the interface copper/graphite/pyrolitic carbon, as measured by us at a maximum load of 0.005 A, showed that there was no need for different contact when polarizing and measuring the anode potential. As the cathode we used a platinum grid beneath the end of the graphite electrode. When the electrode had been imbedded in teflon, the graphite was purified anodically in a 1 M solution of H_3PO_4 at a current density of $2 \cdot 10^{-5}$ A/cm^2 for 10 h, i.e., until such time as reproducible i-φ curves were obtained over the current density interval $1.5 \cdot 10^{-7}$-10^{-4} A/cm^2.

---

* The specimens of pyrolytic carbon were kindly supplied by A. I. Baver and M. I. Chaikan.

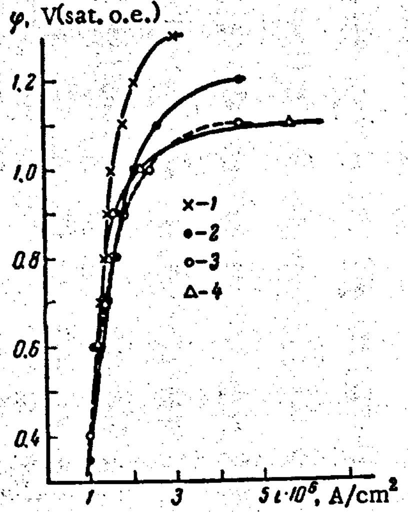

Fig. 1. Graphite electrode potential as a function of current density in 1 M phosphate buffer solutions at different pH: 1) 1, 2) 3, 3) 7, 4) 9.

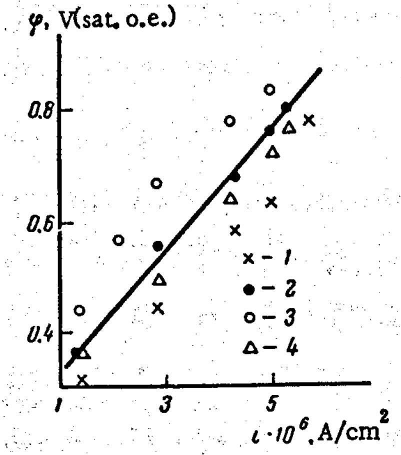

Fig. 2. Graphite electrode potential as function of the current density in 1N KCl solution for different pH: 1) 1; 2) 2; 3) 4.8; 4) 0.

Plotting of the polarization curves was preceded by anodic activation in a corresponding solution by a current $2 \cdot 10^{-5}$ A/cm² for 15 min, after which the solution was replaced by another portion of the same composition in which we carried out the polarization measurements. Each point on the curve was held for twenty minutes until we obtained a constant potential. This insured reproducibility of the i-φ curves later obtained. The phosphoric acid and potassium and sodium phosphates used in our work were recrystallized from doubly distilled water two times and cleaned anodically on platinum just before the curves were plotted, while the hydrochloric and chloric acids were doubly distilled.

Results of the measurements of current as a function of potential in phosphate and chloride solutions with different pH are shown in Figs. 1 and 2. It follows from Fig. 1 that the slight variation in current density considerably changes the electrode potential, with the linear dependence of the current on potential being maintained over an interval of almost one volt.

The polarization curves obtained during transition from large to small densities are close to the results obtained when the current density is increased. For practical purposes the electrode potential is not a function of the mixing (2,000 rpm).

Stability of the potential with time and coincidence of the i-φ curves during their forward and reverse paths show that the dependence obtained corresponds to the standard process of oxygen generation, and not to charging of the electrode. Approximate calculations show that under our conditions the electrode holding time at constant potential is considerably greater than the time required to establish an oxygen coating on the electrode that does not vary with time.

As shown in Fig. 1, the increase in pH from 1 to 9 causes virtually no change in the behavior of the i-φ curve. Figure 2 shows polarization curves in HCl and KCl solutions for the same potential region. These data relate to the generation of oxygen rather than chlorine since the electrode potential is at least 0.3 V more negative than the equilibrium chlorine electrode potential.

As can be seen from the graph, there is no qualitative difference from the relationship obtained earlier for phosphoric acid, although in chloride solutions the straight lines are less steep. Nonindependence of pH is observed over the pH interval from 0 to 2; at pH 4.8 the curve rises a little higher than for other solutions and is no longer a straight line. Similar measurements were cited by us for perchlorate solutions, however in that case we observe very strong hysteresis at low potentials and the data are poorly reproducible.

During polarization of the electrode in the linear region of the i-φ curve the potential is set up within one or two minutes and on further polarization, in the region 1-1.2 V the charging of the electrode until a stationary potential takes three to four hours. In the event that this potential is obtained from the higher current densities, it is set up considerably more quickly. In the transition region we observe hysteresis in the forward and reverse paths of the i-φ curve. An increase in the electrode potential above 1.3 V (sat. o.e.) results in a Tafel dependence between the current and potential. Data relating to this region will be considered by us in separate communications.

Apart from the stationary polarization curves, we determined the capacitance for the initial segment of the potential drop curve. The capacitance was calculated from the drop curves obtained by means of a C1-4 electronic oscillograph by the method described earlier in [6].

The capacitances obtained are 3,000–4,000 $\mu F/cm^2$ of visible surface in acid solutions (pH 1–4.5). In the alkaline region at pH 9 the capacitance is 50–60 $\mu F/cm^2$ of visible surface. Taking it into account that the electrode surface is bumpy, we should take the roughness factor as approximately equal to 3, though in actual fact, considering the microrelief, it is most likely greater. In this case the capacitance derived by us in the alkaline region is close to the double layer capacitance.

DISCUSSION OF RESULTS

Oxygen generation on graphite is a complex and multistage process. The first stage is in all likelihood an OH^- discharge (or H_2O molecule) with the formation of an adsorbed OH radical or atomic oxygen, for example,

$$C + OH^- \rightarrow C(OH)_{ads} + e^- \tag{1}$$

or

$$C + OH^- \rightarrow C(O)_{ads} + H^+ + 2e^-. \tag{2}$$

Further removal of the oxygen may take one of three paths: O_2, CO or CO_3, with each of the products being formed through different mechanisms. In the region we investigated the generation of free oxygen as a basic product over the whole potential interval is extremely unlikely since we are basically operating at potentials more negative than the equilibrium oxygen potential for the given solution, the difference attaining 0.5 V.

The C/CO equilibrium potential is +0.51 V for the hydrogen electrode in the same solution, and +0.21 V for the C/CO_2 electrode [7]. Thus, the formation of both products is thermodynamically possible, although formation of CO_2 is more likely since the CO_2 equilibrium potential is considerably below that of CO.

It is known from numerous published data that during oxidation of ordinary graphite in an alkaline medium at potentials 0.9–1.1 V (sat. o.e.), or in an acid medium at more positive potentials, CO_2 is formed more readily and CO and organic compounds containing oxygen are obtained in relatively small quantities (see, for example, [1]).

The actual formation of the CO_2 may take place chemically, for example

$$2C(O)_{ads} \rightarrow C + CO_2, \tag{3}$$

or electrochemically, for example,

$$C(O)_{ads} + OH^- \rightarrow CO_2 + H^+ + 2e^- \tag{4}$$

or

$$C(OH)_{ads} + OH^- \rightarrow C(OH)_{2\,ads} + e^- \rightarrow CO_2 + 2H^+ + 3e^-. \tag{5}$$

Reactions (3)–(5) are possible systems, the number of which can be enlarged.

Observance of the linear dependence of the current on potential over as wide an interval as this and the absence of any great dependence of the current on the pH of the solution are effects for which for the time being it is difficult to given an exhaustive interpretation.

It is quiet clear that the coating of the surface with oxygen over a wide range of potentials cannot remain small the whole time. There are no quantitative data on the adsorption of oxygen under out experimental conditions, hence on analogy with other cases it may be considered that adsorption of the oxygen as a first approximation can be described by the logarithmic isotherm

$$\theta = \theta_p + \frac{nF}{r}\eta, \tag{6}$$

where θ is the coverage for the overvoltage η, θ_p is the same at equilibrium potential, r is the coefficient in Eq. (7) relating the bond energy of the adsorbed oxygen and the degree of coverage

$$E = E_0 - r\theta. \tag{7}$$

If the adsorbed particle is atomic oxygen, then n = 2 (reaction (2)) and if the radical is hydroxyl, then n = 1 (reaction (1)). Equation (6) presupposes that the energy level of the adsorbed oxygen is determined entirely by the overvoltage, i.e., that the equilibrium discharge-ionization occurs.

The overvoltage is associated with the potential φ, the standard equilibrium potential φ_p^0 and the concentration of OH ions by the following relationship

$$\eta = \varphi - \varphi_p{}^0 + \frac{RT}{F}\ln c_{OH^-}. \tag{8}$$

Variation in the carbon-oxygen bond energy during variation in the degree of coverage leads to variation in the activation energy of the second stage of the electrode process—removal of the adsorbed oxygen. In the case of reactions involving electrochemical desorption of CO_2 (reactions of the type (4) or (5)) we can expect that the more firmly the oxygen and hydrogen are bonded the lower the activation energy will be. Accumulation of oxygen on the surface leads to weakening of its bond with the carbon and, therefore, to increased activation energy. Variation in the activation energy due to change in the coverage may be represented, on analogy with other known cases, as

$$\Delta E^* = -\alpha\Delta E = \alpha r \Delta\theta. \tag{9}$$

This quantity depends upon the potential and composition of the solution

$$\Delta E^* = \alpha n F \Delta\varphi + \alpha n RT \Delta \ln c_{OH^-}. \tag{10}$$

Here α is the transport coefficient for electrochemical desorption of the CO_2 (discharge of OH^- or H_2O alongside the adsorbed oxygen or hydroxyl with the formation of a complex which then becomes gaseous CO_2).

The rate of this reaction is proportional to the concentration of adsorbed oxygen and discharging particles, and depends exponentially on the potential and on variation in the activation energy due to variation in the bond energy

$$i = k\theta c_{OH^-}\cdot e^{-\Delta E^*/RT}\cdot e^{\alpha\Delta\varphi F/RT} = k\theta c_{OH^-}^{1-\alpha n}\cdot e^{\alpha(1-n)\Delta\varphi F/RT}. \tag{11}$$

Linear dependence on potential has been observed experimentally. The dependence results from Eq. (11) at n = 1, since θ depends linearly on the potential. In other words at n = 1 (OH radicals are adsorbed on the surface) the accelerating effect of the potential on the CO_2 electrochemical desorption reaction is compensated by its retarding effect through an increase in the surface coverage, as a result of which the C—OH bond is weakened and the reaction activation energy increased. As a result, dependence of the current on the potential is determined by dependence of the current on coverage.

The practical nondependence of the current on concentration of the alkali follows from Eq. (11) on conditions that $\alpha n = 1$, i.e., taking it than n = 1, we should get $\alpha = 1$. Thus, the nature of the dependence of current on c_{OH^-} may be explained by assuming that the reaction of the electrochemical desorption of CO_2 involving the OH^- ions is barrier-free. For determination of the barrier-free reaction see [8].

Typical of a barrier-free discharge is proportionality of the OH ions concentration current at a constant electrode potential. In the given case this effect is compensated by the influence of the c_{OH^-} on coverage and, therefore, on the bond energy and activation energy.

The quantity θ depends on c_{OH^-}, but the dependence is less pronounced (linear dependence of θ on c_{OH^-}) so that in accordance with the experimental data the current can be considered to depend hardly at all on the OH^- concentration.

From Eq. (6) it is easy to find the adsorbed pseudo-capacitance

$$C_{ps} = n\cdot NF\frac{\partial\theta}{\partial\eta} = \frac{n^2NF^2}{r}, \tag{12}$$

where N is the maximum possible oxygen adsorption $N \approx 2 \cdot 10^{-9}$ g·at/cm^2.

It has been experimentally found that $C = 10^3$ microfarads/cm^2, if we make allowance for only approximate roughness of the surface. When the microrelief is taken into account the capacitance is approximately $3 \cdot 10^2$ μF/cm^2. From here we calculate $r = 15$ kcal/mole, i.e., we obtain a quantity of the same order as the order as the ordinary value of r for other cases in which the logarithmic adsorption isotherm is observed.

From Eq. (12) it follows that the pseudo-capacitance is constant over a certain potential interval where the initial Eq. (6) is valid. As is known, the logarithmic adsorption isotherm is only observed at mean coverages, usually over a range of θ from 0.2 to 0.8. This corresponds, given the value of r as estimated above, to a constant pseudo-capacitance over the interval of about 0.4 V. This conclusion also accords with experiments.

Thus, we have explained the experimental data by assuming that removal of the oxygen from the graphite surface occurs in the form of CO_2 by means of barrier-free electrochemical desorption.

The actual possibility of this process occurring seems quite reasonable in the case in point since it is favored by a low anodic potential and the electrode reaction should be greatly decelerated.

It is not out of the question, however, that there is another mechanism in which $\alpha < 1$, if we accept that at the slow stage of the reaction not one but two electrons are transported. The kinetic equation corresponding to this process can be written in the form

$$i = k\theta c_{OH^-} \cdot e^{-\Delta E^*/TR} \cdot e^{\alpha 2\Delta\varphi F/RT} = k\theta c_{OH^-}^{1-\alpha n} \cdot e^{\alpha(2-n)\Delta\varphi F/RT}. \tag{13}$$

This equation accords with experimental data at $n = 2$ and $\alpha = 1/2$. Formally accordance with the experiments is just as satisfactory, but physically the first explanation, which does not require supposition of the simultaneous transition of two electrons, is more likely to be true.

Supposition of the discharge of H_2O molecules, which at first glance seems most apt as an explanation of the nondependence of current on pH, does not produce in actual fact any satisfactory results. For example, if we take the oxygen coverage of the surface to be small, we cannot derive an equation giving a linear dependence of i-φ over a wide range of potentials. But if we consider that adsorption of the oxygen conforms to the logarithmic isotherm (6), then we get

$$i = k\theta e^{-\Delta E^*/RT} \cdot e^{\alpha\Delta\varphi F/RT} = k\theta c_{OH^-}^{-\alpha n} \cdot e^{\alpha(1-n)\Delta\varphi F/RT}. \tag{14}$$

This equation tallies with experimental data only at $\alpha = 0$, i.e., it requires the most unlikely supposition that there is discharge of the water without activation energy.

We should also point out that the assumption of slow electrochemical desorption of O_2 is in itself improbable and means a change of sign in Eqs. (9) and (10) (weakening of the C–O bond reduces the activation energy of desorption of O_2) and, consequently, the derived kinetic equations cannot be made to agree with experimental data, whatever the parameters.

Finally, the observed dependences cannot be explained by the slowness of any chemical stage of the type of reaction (3). The activation energy of this stage should depend to a considerable degree on the CO bond energy, i.e., on θ and in the final analysis on φ. Consequently, we should not observe a linear but an exponential dependence of i on φ and substantial dependence by the current on c_{OH^-}.

A linear dependence of i-φ, on condition that the current is not a function of the pH, could be obtained by assuming that detachment of CO molecules is the slow stage. It was noted earlier that this process is most likely not the principal one. Furthermore, experimental data may be made to agree with this mechanism only if we accept the not very valid assumption that the activation energy of the formation of CO molecules from $C(O)_{ads}$ does not depend on the energy of the oxygen and carbon adsorption bond.

Thus, although the explanation given above—barrier-free electrochemical desorption of CO_2 through the discharge of an OH^- ion—has not been conclusively proved, it still is the most acceptable version of those considered.

LITERATURE CITED

1. V. S. Stender, Electrolytic Production of Chlorine and Alkalis, [in Russian], ONTI, Khimteoret, Leningrad (1935).
2. H.T. Thiele, Trans. Faraday Soc., 34, 1033 (1938).
3. A. Hicling and S. Hill, Disc. Faraday Soc., 1, 236 (1947).
4. A. R. G. Brovn, A. R. Hall, and W. Watt, Nature, 172, 1145 (1953),
5. A. S. Fialkov and A. I. Baver, et alia, Uspekhi khimii, 34, 132 (1965).
6. V. É. Plast and Z. A. Iofa, Zh. fiz. khimii, 33, 913 (1959).
7. V. Latimer, Oxidation States of Elements and Their Potentials in Aqueous Solutions [in Russian], For. Lit. Press, Moscow (1954).
8. L. I. Krishtalik, Zh. fiz. khimii, 34, 117 (1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
