505. *Depolarisation by Oxygen and by Hydrogen Peroxide at Graphite Cathodes in Alkaline Solutions.*

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Re-examination of the equilibrium between oxygen and alkaline peroxide solutions at spectroscopically pure graphite electrodes in the form of short cylindrical rods confirms earlier results. On cathodic polarisation, the potential depends markedly on the rate of stirring of the electrolyte, and in 1·0M-sodium hydroxide vigorously stirred with oxygen the current–potential curve reveals two distinct depolarisation stages before hydrogen is evolved. The first corresponds to the almost quantitative reduction of oxygen to hydrogen peroxide, and the second to reduction of the latter. With previously heat-activated electrodes, however, the potential was independent of stirring, and the yield of peroxide was only 35—45% of theory. Some aspects of the reduction mechanisms and their analogy to those accepted to account for the phenomenon observed at the dropping-mercury cathode are discussed.

THERE is little information about the rôle of depolarisation by oxygen and hydrogen peroxide of graphite cathodes in alkaline solution. Such as there is is difficult to compare owing to the ill-defined nature of the carbons used and the widely different methods of pre-treatment and their effect on the yield of peroxide produced cathodically; also the form of electrode which would permit adequate interpretation of the results is in doubt.[1] With graphite electrodes, in the form of hollow blocks through which oxygen was forced, Berl[2] showed that the equilibrium $O_2 + H_2O + 2e \rightleftharpoons OH^- + HO_2^-$ could be readily established at purely graphite surfaces or surfaces covered with activated carbon, although

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[1] Herbert, "Zur Frage des Brennstoffelementes," Diplomarbeit, Darmstadt, 1928; Skumburdis, *Kolloid Z.*, 1931, **55**, 156; E. Berl, *Trans. Electrochem. Soc.*, 1939, **76**, 359; Brushtein and Frumkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 327; Shigeru and Mizuno, *Bull. Tokyo Inst. Technol.*, 1948, **13**, 102.

[2] W. G. Berl, *Trans. Electrochem. Soc.*, 1943, **83**, 253.

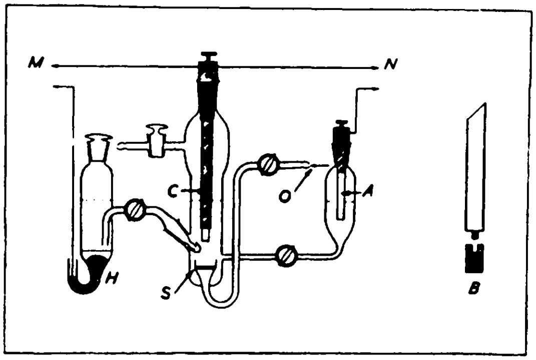
the two types of surface gave very different yields of hydrogen peroxide during cathodic polarisation; the former produced insignificant amounts and the latter almost 100% yield over a wide range of current density. Weizse and Jaffe[3] confirmed Berl's results and inferred that in both acid and alkaline air-depolarised cells hydrogen peroxide is catalytically decomposed. Regarding the mechanisms, Yeager *et al.*[4] showed that peroxide is formed on carbon electrodes in alkaline solutions rapidly and reversibly through the cathodic reduction of adsorbed oxygen, but Bratzler[5] postulated an oxonium salt-like structure as intermediate and the participation of atomic hydrogen produced by the primary discharge process. No result on the electroreduction of peroxide at graphite electrodes seems to have been published.

We used a simple spectroscopically pure graphite electrode to examine the equilibrium between oxygen and alkaline peroxide solutions, and the rôle of depolarisation by oxygen at 1 atm. and by hydrogen peroxide at different concentrations. Preliminary results about the effect of the state of the surface on the course of the reduction of oxygen and the yield of peroxide are also reported.

EXPERIMENTAL

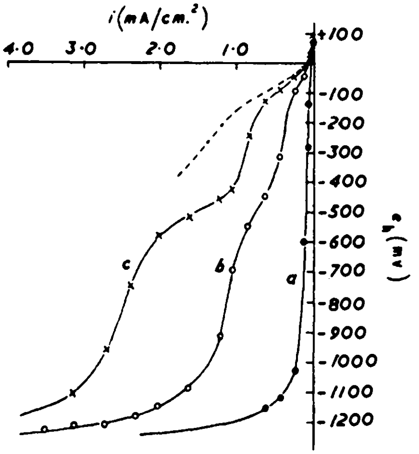
Electrodes.—Spectrographically standardised graphite (Johnson and Matthey) was used, supplied as cylindrical rods 30 cm. long and 6·5 mm. in diam. About 10 cm. lengths were protected in tightly fitting Polythene tubing except for a length of *ca.* 2 cm. left uncovered to serve as electrode. The electrodes were boiled with 4N-hydrochloric acid, rinsed with water, and then boiled with dilute sodium hydrogen carbonate solution. The surface was then left untouched, and when not in use the electrodes were kept under distilled water.

FIG. 1.



C, Cathode; *H*, saturated calomel half-cell; *A*, auxiliary graphite anode; *O*, entry for pure oxygen; *S*, sintered glass disc; *M*, *N*, connections to potentiometer and polarising circuits, respectively.

FIG. 2. *Current–potential curves obtained in* 1·0M-*sodium hydroxide with the electrolyte* (*a*) *stagnant and* (*b*) *moderately and* (*c*) *vigorously stirred with oxygen.*



Materials.—Inhibitor-free hydrogen peroxide was prepared from 40% sulphuric acid and sodium peroxide (B.D.H.).[6] The product after two distillations over silver sulphate varied in concentration from 1·0 to 3·0M and was used as a stock. Sodium hydroxide solutions were prepared by dilution of a carbonate-free concentrated solution of "AnalaR" solid. Water was twice distilled over alkaline permanganate.

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[3] Weizse and Jaffe, *Trans. Eletrochem. Soc.*, 1948, **93**, 128.

[4] Yeager, Witherspoon, Urbach, Yeager, and Hovorka, Tech. Report No. 4 (Second series) to the Office of Naval Research, Washington, October 1954.

[5] Bratzler, *Z. Elektrochem.*, 1950, **54**, 81.

[6] Kilpatrick, Reiff, and Rice, *J. Amer. Chem. Soc.*, 1926, **48**, 3019.

Analysis.—Peroxide was determined colorimetrically with a Hilger absorptiometer, a 2% solution of " AnalaR " titanyl potassium oxalate in 5N-sulphuric acid being used as reagent. With 5N-sulphuric acid as diluent, use of a 1 cm. cell and a Hilger No. 1 blue filter gave a linear (±3—5%) density–concentration curve from 20 to 80 mg. $l.^{-1}$ of peroxide.

Electrical Measurements.—Polarisations were carried out in a Pyrex glass cell (Fig. 1). For open-circuit measurements the auxiliary anode side compartment was omitted. All measurements were made at 25° ± 0·1° (air thermostat). Potentials were recorded with a circuit incorporating a Ferranti electrometer valve and a Tinsley potentiometer of range 0—1·9 v. Polarisation current was supplied by a dry battery and recorded on an Onwood microammeter in parallel with a Tinsley universal shunt. All potentials e are against the saturated calomel electrode, e_0 for which is taken as 0·245 v on the hydrogen scale.

RESULTS AND DISCUSSION

A graphite electrode in equilibrium with oxygen and alkaline peroxide solutions:

$$O_2 + H_2O + 2e \rightleftharpoons HO_2^- + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

should set up a potential

$$e = e_0 + (\boldsymbol{RT}/2\boldsymbol{F}) \ln \{[p(O_2) \, . \, a(H_2O)/[a(OH^-) \, . \, a(HO_2^-)]\} \quad . \quad . \quad . \quad (i)$$

where $a(x)$ denotes the activity of species x. With $p(O_2) = 1$ atm. and $a(H_2O)$ taken as unity, a plot of e against $\log [a(OH^-) \, . \, a(HO_2^-)]$ should be straight with slope −0·0296 v at 25° and intercept e_0. Our results (Table 1) confirm this. At these concentrations $a(HO_2^-)$ was taken as equal to the concentration of peroxide x as determined analytically, and $a(OH^-)$ to the activity of the original alkali minus x. Eqn. (i) can then be put as

$$e = e_0 - (\boldsymbol{RT}/2\boldsymbol{F})\{\ln [a(OH^-)_{\text{original}} - x] + \ln x\} \quad . \quad . \quad . \quad . \quad (1)$$

which on differentiation with respect to x gives

$$\mathrm{d}e/\mathrm{d}x = (\boldsymbol{RT}/2\boldsymbol{F})\{1/[a(OH^-)_{\text{original}} - x] - 1/x\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From eqn. (2), a plot of e against x for one alkali concentration should give a curve having a minimum at $a(OH^-)_{\text{original}} = 2x$, as was substantiated from measurements in 0·1M-sodium hydroxide containing various concentrations of peroxide.

Although this interpretation differs from Berl's, our simple working electrode gives results in agreement with it. However, we obtain $e_0 = -49 \pm 3$ mv, as compared with Berl's value (on our sign convention) of −41·6 mv. For reaction (*a*) our value gives $\Delta G°(HO_2^-) = -16·8$ kcal. $mole^{-1}$, which is at least 1 kcal. higher than the usual values. [In this calculation we use the value $\Delta G°(OH^-) = -37·595$ kcal. $mole^{-1}$.[7]]

TABLE 1. *Potential of the graphite electrode as a function of the peroxide ion activity at 25° in solutions saturated with 1 atm. of oxygen.*

$a(HO_2^-)$	$a(OH^-)$ *	$\log [a(OH^-) . a(HO_2^-)]$	e_h (mv)	$a(HO_2^-)$	$a(OH^-)$ *	$\log [a(OH^-)a(HO_2^-)]$	e_h (mv)
		0·1M-NaOH				1M-NaOH	
0·0007	0·0760	−4·2741	79	0·0006	0·699	−3·3773	50
0·0008	0·0758	−4·2172	73	0·0008	0·658	−3·2787	46
0·0013	0·0807	−3·9792	68	0·0010	0·671	−3·1733	43
0·0034	0·0755	−3·5906	57	0·0015	0·684	−2·9888	35
0·0050	0·0678	−3·4698	53	0·0028	0·662	−2·7319	31
0·0104	0·0626	−3·1864	44	0·0046	0·708	−2·4872	29
0·0259	0·0515	−2·8749	31	0·0101	0·655	−2·1795	15
0·0379	0·0410	−2·8086	29	0·0610	0·625	−1·4188	−10
0·0570	0·0204	−2·9345	34				

* Obtained from activity coefficients given by Harned and Owen (" The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 560).

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[7] Latimer, " Oxidation Potentials," Prentice-Hall, Inc., New York, 2nd edn., 1953, p. 39.

Although equilibrium was established almost instantaneously in oxygen-stirred solution of alkali containing peroxide, in the absence of peroxide the initial potential drifted and steady values of +40—+60 mv in 1·0M-sodium hydroxide were obtained only after 30—40 min. On cathodic polarisation at gradually increasing current densities, the potential of the electrode changed in a manner which depended greatly on the rate of stirring of the electrolyte (Fig. 2). With the stagnant electrolyte relatively small currents shift the potential to a resting stage which corresponds presumably to evolution of hydrogen. In the stirred electrolyte, however, two distinct depolarisation stages which indicate two different reduction processes occur before hydrogen begins to be evolved. In vigorously stirred electrolyte, the limiting current density, i_L, for the first reduction stage is about 0·8 mA /cm.^{2} of the geometrical surface area. From current-efficiency experiments (Table 2) this stage was shown to correspond to the reduction of oxygen almost quantitatively to hydrogen peroxide on the assumption of a two-electron transfer in the overall reaction. Results in Table 2 show that peroxide could also be formed at a pure graphite surface not previously activated with a current efficiency which, within the limits of accuracy of analysis, approximates to 100%; this result differs from that found by Berl.[2]

FIG. 3. *Current–potential curves obtained in* 1·0M-*sodium hydroxide vigorously stirred with oxygen with* (*a*) 0·0021, (*b*) 0·0092, *and* (*c*) 0·0180 *moles l.*$^{-1}$ *of hydrogen peroxide.*

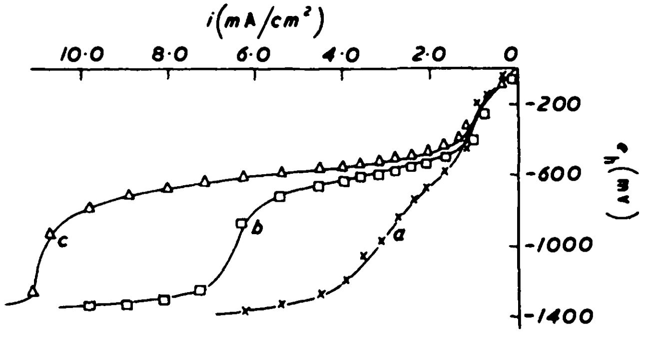

TABLE 2.

Time (min.)	Current density (μA/cm.^{2})	$-e_h$ (mv) * Initial	$-e_h$ (mv) * Final	H_2O_2 yield (mg. l.$^{-1}$) Found †	H_2O_2 yield (mg. l.$^{-1}$) Calc.	Efficiency (%)
90	588	115	118	69	70	98·5
90	588	117	116	67·2	70	96·0
180	588	116	120	137·6	140	92·8
180	588	112	117	130	140	92·8
90	1034	183	196	116	123	94·3
150	1034	186	200	189	205	92·7

* Electrode potential relative to the hydrogen electrode.
† Average from at least two analyses.

That the second depolarisation stage corresponds to the reduction of H_2O_2 (or·HO_2^-) is shown by Fig. 3. The oxygen wave remains almost unaffected while the second wave becomes more stretched with the increase of peroxide concentration in such a manner that i_L(total) − $i_L(O_2)$ is almost proportional to [H_2O_2]. With pure hydrogen instead of oxygen the first wave disappeared completely and the potential fell directly to that of the second reduction stage. Under such conditions the above proportionality [with $i_L(O_2) = 0$] holds.

A pure graphite surface seems so far to be the only solid electrode on which the reduction wave of both oxygen and hydrogen peroxide in alkaline solutions can be reproduced almost quantitatively as with a dropping-mercury cathode.[8] (With a rotating gold micro-electrode the hydrogen peroxide wave was ill-defined, and with an amalgamated silver electrode the waves were not reproducible.[9]) However, even on graphite the reduction mechanism is complex; thus for the oxygen-reduction step under limiting-current conditions, the equation

$$i_{\mathrm{L}} = n\,\mathbf{F}DC_0/\delta \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (b)$$

(where n is the number of electrons involved $= 2$, D is the diffusion coefficient of oxygen $= 2{\cdot}6 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[10] C_0 the bulk concentration of oxygen in 1·0M-NaOH $= 8{\cdot}3 \times 10^{-7}$ mole cm.$^{-3}$ [11]) gives for δ, the thickness of the diffusion layer, $5{\cdot}2 \times 10^{-3}$ cm., a value of the same order of magnitude as those obtained polarographically under similar conditions of stirring.[12] A plot of e_{h} against $\log[(i_{\mathrm{L}} - i)/i]$ [13] yields, however, a straight line with slope 80—90 mv, which shows that the polarisation observed is not a purely concentration one, and that reduction does not proceed rapidly in one act according to $O_2 + H_2O + 2e \longrightarrow HO_2^- + OH^-$; the primary slow discharge of diffusing oxygen may be rate-determining. The state of the surface appears to be of primary importance in this respect. With short pieces of graphite previously heated under vacuum for about 2 hr. at 800—900°, then fitted as shown in Fig. 1, *B* to serve as electrodes, the course of oxygen reduction in oxygen-saturated 1·0M-sodium hydroxide differed fundamentally from that described above in that the potential during cathodic polarisation was independent of the rate of stirring of the electrolyte, although the general trend of the current–potential curve (broken curve in Fig. 2) was essentially the same as that obtained with the untreated electrode in the vigorously stirred electrolyte, and the yield of peroxide varied between 35 and 45% only of theory. At such a surface the reduction is probably of adsorbed oxygen to form adsorbed HO_2 radicals which may then undergo self-terminating chain reactions [14] leading to low peroxide yields. On untreated and heat-activated graphite surfaces the course of oxygen-reduction can be visualised as follows:

On untreated surface

$$O_2(\text{diffusing}) + e \longrightarrow O_2^- \ (\text{slow})$$
$$O_2^- + H_2O + e \longrightarrow HO_2^- + OH^-$$

On heat-activated surface

$$>O_2(\text{adsorbed}) + e \longrightarrow >O_2^-(\text{adsorbed}) \ (\text{slow})$$
$$>O_2^- + H_2O \longrightarrow >O_2H + OH^-$$
$$2>O_2H + OH^- \longrightarrow HO_2^- + H_2O + O_2$$

or

$$2>O_2H \longrightarrow H_2O + 1\tfrac{1}{2}O_2$$

The half-wave potential of the peroxide wave lies (Fig. 3) at about —0·630 v, which is in close agreement with that reported by Bockris *et al.*[15] from measurements with the dropping-mercury cathode. For the three peroxide concentrations used the i_{L} values as calculated on the basis of equation (*b*) are roughly twice those obtained experimentally. We do not yet know whether the mechanism suggested by Bockris *et al.* to account for the splitting of the peroxide wave at mercury would still be applicable at graphite.

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