GENERATION OF HYDROGEN PEROXIDE BY REDUCTION OF OXYGEN IN SEMIHYDROPHOBIC TRICKLE ELECTRODES

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The reduction of oxygen to hydrogen peroxide was studied in semihydrophobic trickle electrodes prepared from crushed graphite and teflonized carbon black. The potential of these electrodes was found markedly more positive and the peroxide current yields appreciably higher than for electrodes made of used crushed graphite. The reason for this is the higher surface area of the electrodes containing carbon black and occurrence of a three-phase interface in them. The relevant properties, i.e. electric resistance, electrolyte holdup, polarization curves for the oxygen reduction and pexide current yields, were also studied for trickle electrodes containing graphite felt. The electrochemical activity of electrodes made from untreated felt was found rather low but it increased several times when felt pretreated by oxidation was used.

It has been found[1-4] that reduction of oxygen in crushed graphite trickle electrodes is associated with the generation of hydrogen peroxide in relatively high current yields. The potential of such electrodes, however, decreases markedly with increasing current density, particularly due to a limited rate of oxygen transport through the electrolyte layer trickling down the surface of the electrode material particles[5]. As a result, increase in the current density is accompanied by increasing losses of the peroxide by reduction and decreasing current yields of its formation.

Unlike these trickle electrodes, gas diffusion electrodes possessing semihydrophobic structure involve a well-developed three-phase boundary, owing to which the rate of oxygen reduction is higher and their potentials are more positive. Thus, at identical current densities and peroxide concentration in solution, the peroxide current yields are higher in gas diffusion electrodes[6] than in crushed graphite trickle electrodes[3].

On the other hand, gas diffusion electrodes, particularly ones large in size, have some disadvantages hindering their large-scale use, such as a poorer mechanical stability and limited lifetime.

The first part of this work therefore concentrated on trickle electrodes which, for attaining a larger electrochemically active area, contain not only graphite but also a hydrophobic component, viz. teflonated carbon black. We attempted to prepare electrode materials containing graphite particles coated by a layer of carbon black, which is a suitable material for hydrogen peroxide formation[9].

The possibility of preparing peroxide in carbon black-containing trickle electrodes has been studied by McIntyre and Phillips[7]. The electrode potentials achieved by them, however, were rather negative and peroxide current yields were low. At a current density of 465 A/m^2, the potential was −1·2 V vs silver/silver chloride electrode and the peroxide current yield was 27%.

Another material employed by us was graphite felt. Assets of this trickle electrode material include easy preparation of the electrode, high surface area, against crushed graphite and elimination of the hazard of the membrane being cut by the electrode material.

EXPERIMENTAL

For preparing the trickle electrode material, 3 g of carbon black was wetted with approximately 3 ml of ethanol and mixed with 100 ml of distilled water, 30 g of crushed graphite (0·63—1·00 mm grain size) was poured into this system, and teflon dispersion was added dropwise. The slurry was filtered out, dried at 110°C and sintered for 30 min at 350°C. The material containing 10 wt. % teflon was disintegrated, and the 0·63—1·25 mm sieve fraction was used as the trickle electrode packing. The layout of the trickle electrode electrolyzer has been reported previously[3]. For graphite felt electrodes, GFA 5 graphite felt (Sigri, F.R.G.) 5 mm thick was compressed between the cathode collector plate and a diaphragm to a final thickness of 3·3 mm.

Electrolysis was performed using a Bären diaphragm (Akkumulatorenfabrik Dr Jungfer, Austria) of 0·2 mm thick, or a Nafion 295 ionex membrane (Du Pont). When using the diaphragm, a mixture of oxygen with 2M-NaOH was fed into the upper part of the cathode compartment; the anode compartment was closed. When using the ionex membrane, this solution was fed to the bottom of the anode compartment and let out at the top of the anode compartment to the injector, where it was mixed with oxygen and fed into the cathode compartment. The total alkalinity of the outflowing solution, i.e. the sum of concentrations of hydroxyl and perhydroxyl ions, was about 2 mol/dm^3 in either case.

The stainless steel plate forming the cathode wall was cooled from outside with water so as to keep the temperature inside the electrolyzer at 25 ± 1°C.

The trickle electrode potential was measured using probes located 50, 250 and 450 mm from the gas and electrolyte inlet into the electrode[4]. The trickle electrode potentials reported in the present paper (vs a mercuric oxide electrode in 2M-NaOH) are those measured near the diaphragm, where they attained the most negative values. The polarization curves for the oxygen reduction were measured either at the atmospheric pressure at the electrode outlet or at an outlet overpressure of 0·2 MPa.

The temporary electrolyte holdup in the electrodes was calculated from the volume of the electrolyte (2M-NaOH) that left the trickle electrode in 10 min after discontinuing the current supply and electrolyte feed. Permanent holdup was calculated from the weight difference of the wet electrode material after the temporary holdup measurement and after washing the material and drying it at 105°C. The holdup values express the ratio of the retained electrolyte volume to the total pore volume in the electrode, the latter being calculated from the mean bed density and the density of carbon.

The surface area of crushed graphite was evaluated from the electrode double layer capacity, which was obtained based on measurement in 1M-H_2SO_4 at a linearly increasing and decreasing potential over the region of 0·27 to 0·43 V.

RESULTS AND DISCUSSION

The trickle electrodes containing graphite and carbon black were prepared using five types of carbon black (furnace black as well as acetylene black) with highly different specific surface areas and hydrophobicity.

Optical microscopic observations revealed that not all of the graphite grains were covered uniformly by carbon black; some were, some were only partially covered, and some remained uncovered.

Electric resistance measurements in dependence on the compression of the mixture showed that due to the presence of carbon black, the conductivity of these materials was several times lower than that of crushed graphite itself (Fig. 1). The voltage in the solid phase of the carbon black-containing trickle electrode was also measured during the electrolysis. With "rear" current supply (through the metal plate constituting the wall of the trickle electrode), this voltage was rather high (even 0·8 V at 0·5 kA/m^2). Therefore, "front" current supply – by means of a nickel gauze interposed between the electrode and membrane – was applied in the subsequent measurements. In this case the voltage loss in the electrode materials was several tens of millivolts only. From this it follows that the current is brought to the close vicinity of the most current-loaded layer of the trickle electrode.

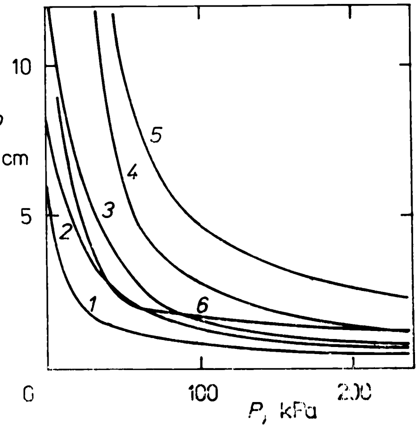

FIG. 1

Dependence of the specific resistance of electrode materials on their compression. *1* S 42 graphite 0·63—1·00 mm grain size, *2* graphite + P 1250 carbon black, *3* graphite + PM 16 E carbon black, *4* graphite + P 1042 carbon black, *5* graphite + Corax 9 carbon black, *6* GFA 5 graphite felt

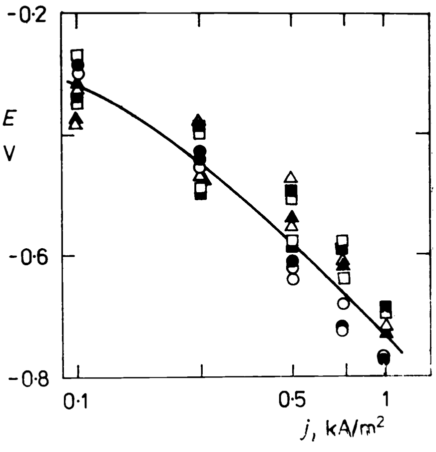

FIG. 2

Polarization curves of oxygen reduction in electrode with P 1042 carbon black, Nafion membrane. Oxygen and electrolyte flow rates (dm^3/h): △ 35, 0·075; □ 35, 0·15; ○ 35, 0·30; ▲ 210, 0·075; ■ 2,01 0·15; ● 210, 0·30

The carbon black hydrophobicity was evaluated by measuring the liquid holdup in the trickle electrode. Table I demonstrates that in the electrode containing P 1250 acetylene black, the volume fraction of pores filled by the electrolyte was very low (both in the temporary and permanent holdups); in electrodes containing P 1042 black and PM 16 E low-surface-area furnace black, liquid pores made up 40–50% of the total pore volume; and in electrodes containing Corax 9 and 600 large-surface-area furnace black, liquid pores represented 63–94% of the total pore volume, which is close to the fraction for crushed graphite.

In the measurement of polarization curves of oxygen reduction, the potentials of the electrode containing the highly hydrophobic P 1250 acetylene black were found very negative (Table II), apparently due to the low fraction of electrolyte in the pores (15–27%) and hence, low fraction of wetted, electrochemically active electrode surface area. Previously we also measured highly negative potentials for gas diffusion electrodes made from this hydrophobic carbon black (−0·8 to −1·0 V at 0·5 kA/m^2). Only after several tens of hours of cathodic polarization, the carbon black surface became partly hydrophilic and the potential reached more positive values (about −0·5 V).

The potential was less negative for trickle electrodes containing graphite and carbon black of other types; it was 0·35 to 0·45 V more positive than that of the crushed graphite electrode. The cause of this apparently lies in the higher specific surface area of the trickle electrodes containing carbon black.

To enable the surface area values of the carbon-black containing trickle electrodes to be compared, we first measured the capacity of the double layer of the electrode made from crushed graphite only. The specific surface area of crushed graphite so obtained, 1·4 m^2/g, corresponds to a specific surface area of $1{\cdot}1 \,.\, 10^4$ cm^{-1}. This is two orders of magnitude higher than the crushed graphite outer surface area (100 cm^{-1}) calculated from the mean graphite particle size and using the surface roughness factor of 2. As we found previously[4], the rate of oxygen reduction increases with the outer surface area of crushed graphite. The data reported indicate that the crushed graphite surface area is primarily determined by the inner pores of the material, although these are not involved in the process of oxygen reduction. The surface area of carbon black, however, can manifest itself in a different manner. Appleby and Marie[8] found that at thin gas diffusion electrodes made from carbon black, the rate of oxygen reduction is directly proportional to the electrode surface area. For the electrodes studied by us, however, the electrochemical activity was in no relation to the specific surface area of the electrode (Tables I and II).

Our data indicate that the electrochemical activity of the electrodes under study is substantially affected by the hydrophobicity of the carbon black, which determines the distribution of the liquid and gaseous phases in the electrode. Furthermore, we found that the potentials of the crushed graphite electrodes and of the electrodes containing carbon black are affected by the gas and electrolyte flow rates in different ways. In the hydrophilic crushed graphite electrodes the potentials are highly dependent on these flow rates, which affect appreciably the mass transport coefficients as well as the gas–liquid interface area[4]. In the electrodes containing also carbon

TABLE I

Basic parameters of trickle electrodes made from S 42 graphite (0·63—1·00 mm) and carbon black or from GFA 5 felt. Oxygen flow rate 35 dm^3/h, solution flow rate 0·075 or 0·300 dm^3/h

Electrode material	Specific surface area $. 10^4 cm^{-1}$	Porosity	Temporary holdup		Permanent holdup
			a	*b*	
S 42 + P 1250	4·8	0·67	0·09	0·21	0·06
S 42 + P 1042	3·5	0·66	0·17	0·26	0·24
S 42 + PM 16E	1·7	0·62	0·22	0·32	0·17
S 42 + Corax 600	8·2	0·61	0·21	0·36	0·42
S 42 + Corax 9	9·1	0·60	0·32	0·48	0·46
S 42	1·1	0·55	0·29	0·42	0·49
GFA 5	—	0·93	0·10	0·19	0·03
GFA 5 oxidized	—	0·93	0·19	0·34	0·04

[a] Solution flow rate 0·075 dm^3/h; [b] solution flow rate 0·300 dm^3/h.

TABLE II

Trickle electrode potentials E and peroxide yields η at 0·5 kA/m^2. Oxygen flow rate 35 dm^3/h, electrolyte flow rates 0·075 to 0·300 dm^3/h

Electrode material	$-E^a$ V	η, %	
		0 MPa	0·2 MPa
S 42 + P 1250[b]	0·95—1·05	7—18	21—39
S 42 + P 1042[b]	0·50—0·76	8—33	20—50
S 42 + PM 16 E[b]	0·50—0·8fl	15—35	36—59
S 42 + Corax 600[b]	0·55—0·8	14—42	21—56
S 42 + Corax 9[b]	0·56—0·75	7—28	16—36
S42[b]	0·93—1·15	2·7—3	6—9
S 42 + P 1 042[c]	0·47—0·64	30—81	35—70
GFA 5[c]	0·76—0·82	65—81	—
GFA 5 oxidized[c]	0·34—0·82	83—85	—

[a] At 0 Mpa; [b] Bären diaphragm; [c] Nafion membrane.

black the potential is influenced by the flow rates to a considerably lesser extent (Fig. 2) – like in gas diffusion electrodes – which is indicative of the existence of a rather stable three-phase boundary.

The peroxide current yields in the electrode containing the hydrophobic P 1250 carbon balck were very low because of the negative electrode potential and the associated peroxide loss by reduction. In the electrode made from the hydrophilic Corax 9 black the peroxide yields were also rather low, which can be explained in terms of a high activity of this carbon black for the decomposition of alkaline solutions of the peroxide (compare with Table I in ref.[9], where this carbon black is labelled I).

The peroxide current yields in all carbon black-containing electrodes were higher than in the electrode containing used crushed graphite (0·63 to 1·00 mm), which is primarily due to the more positive potential values for the former electrodes.

One reason for the more negative potentials of the trickle electrode and lower peroxide current yields occurring when using a diaphragm is the parallel flow of the gas and electrolyte through the anode compartment, which reduces the rate of oxygen transport in the porous electrode[3,4]. A diaphragm further enables transport of the peroxide formed to the anode, whereby a part of the peroxide is lost.

The use of an ionex membrane eliminates the parallel flow of the gas and electrolyte through the anode compartment, the pressure drop is higher and so are the mass transport coefficients in the electrode, and consequently the potentials are more positive. In this arrangement the peroxide current yields are considerably higher (Table II); the peroxide concentrations in the outgoing solution were 0·3 to 1·3 mol/dm^3.

In comparison with gas diffusion electrodes, however, the potentials of the trickle electrodes are more negative (by 0·2 to 0·5 V) and the peroxide current yields are lower. This indicates that the three-phase boundary in the gas diffusion electrode is more expanded than in the trickle electrodes even if containing carbon black of the same kind.

Trickle electrodes made from carbon fiber materials were also studied. A relatively good electric conductivity was found for Sigri graphite felt (Fig. 1), whereas the electric conductivity of carbon tow from various manufacturers (Kuraha, Japan; Monokrystaly Turnov, Czechoslovakia) was about an order of magnitude lower.

The porosity of the trickle electrode containing GFA 5 felt was high. The relative pore filling by liquid (the liquid holdup) was low in this electrode; this applies to both the temporary and permanent holdup (Table I). In view of the fact that graphite felt is completely wetted by aqueous solutions, this indicates that there exists a very thin liquid layer on the surface of the fibers – calculations give thickness of 2 to 4 μm. Using published values of the diffusion coefficient and solubility of oxygen in hydroxide[10], high limiting current densities are obtained for the oxygen reduction per unit superficial surface area of this electrode (8 to 16 kA/m^2). The experimental potentials of oxygen reduction, however, are rather negative at much lower current densities (Fig. 3, curve *1*), giving evidence of marked kinetic hindrance of the reduction at the surface of untreated graphite felt.

For attaining a higher activity of this electrode, the effects of some graphite felt surface treatment procedures were examined. The most effective treatment was shown to be an oxidation of carbon felt in a mixture of sulfuric and nitric acids. The potential of this electrode was significantly higher than that of the electrode made from untreated felt (Fig. 3), and the peroxide current yields were also higher (Fig. 4). At the lowest electrolyte flow rate and at higher current densities, the peroxide current yields could not be measured reliably at the electrode made from oxidized carbon felt because the amount of peroxide formed exceeded its solubility and a suspension containing solid $Na_2O_2.8\,H_2O$ appeared in the trickle electrode space.

The higher activity of the electrode made from oxidized felt is apparently accounted for by the catalytic effect of surface groups (quinone, carboxy, phenol groups) forming on the carbon surface on its oxidation[11-13]. To the positive shift of the electrode potential, obviously also contributes the increased surface area of the felt. We found that oxidation of graphite felt by boiling in the above acid mixture is accompanied by appreciable mass loss (about 26% in an hour of oxidation treat-

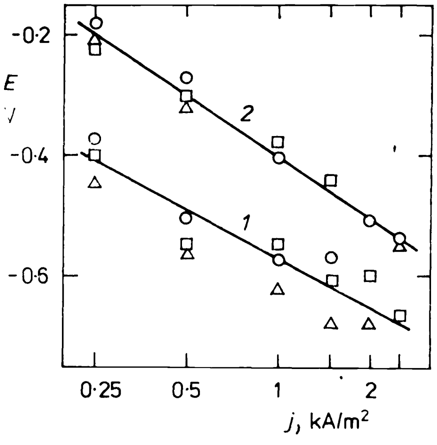

FIG. 3

Polarization curves of oxygen reduction in GFA 5 graphite felt electrode. *1* untreated felt, *2* oxidized felt. Labelling as in Fig. 2

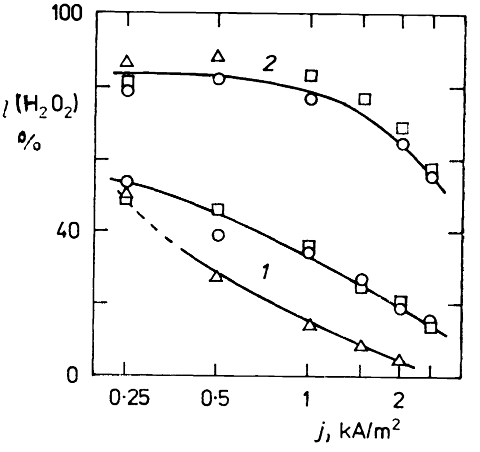

FIG. 4

Peroxide current yields in dependence on current density for GFA 5 graphite felt electrode. Labelling as in Fig. 2

ment). During this oxidation, nonuniform "burnup" of the graphite fiber surface takes place, which, as our scanning microscopic observations revealed, brings about a marked expansion of the fiber surface.

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