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SODIUM PERBORATE PREPARATION BY CATHODIC REDUCTION OF OXYGEN IN A TRICKLE-BED REACTOR

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The preparation of alkaline solution of hydrogen peroxide by cathodic reduction of oxygen in a trickle-bed reactor has been attempted as a first step in the preparation of sodium perborate. The effect of variation of current density, liquid flow rate and concentration of sodium hydroxide on current efficiency of formation of hydrogen peroxide has been studied. Later, attempts have been made to prepare sodium perborate by taking borax in the electrolyte.

Key words: Trickle-bed reactor, hydrogen peroxide, sodium perborate, oxygen reduction

INTRODUCTION

Hydrogen peroxide is prepared both by chemical and electrochemical route. In the latter case, the investigations were carried out by the cathodic reduction of oxygen at solid electrodes [1]. In recent years, three-dimensional electrodes having a high space-time-yield with their high mass-transfer characteristics enabled to employ such electrodes for oxygen reduction[1].

Trickle-bed reactors have been investigated both for chemical and electrochemical syntheses. In these reactors, a co-current flow of gas and liquid through a bed of catalytic or active particles takes place. Use of such trickle-bed reactors has been made in the preparation of H_2O_2 [2-7] and dithionite [2] and detailed characteristics of such trickle bed reactors are also described. In situ preparation of hydrogen peroxide at a cheaper cost compared to the purchased peroxide is reported [5] by using this reactor. The preparation of sodium perborate by cathodic reduction of oxygen has been reported [8]. In another paper [9], the kinetics of oxygen reduction in a mixed borax-sodium hydroxide electrolyte are reported.

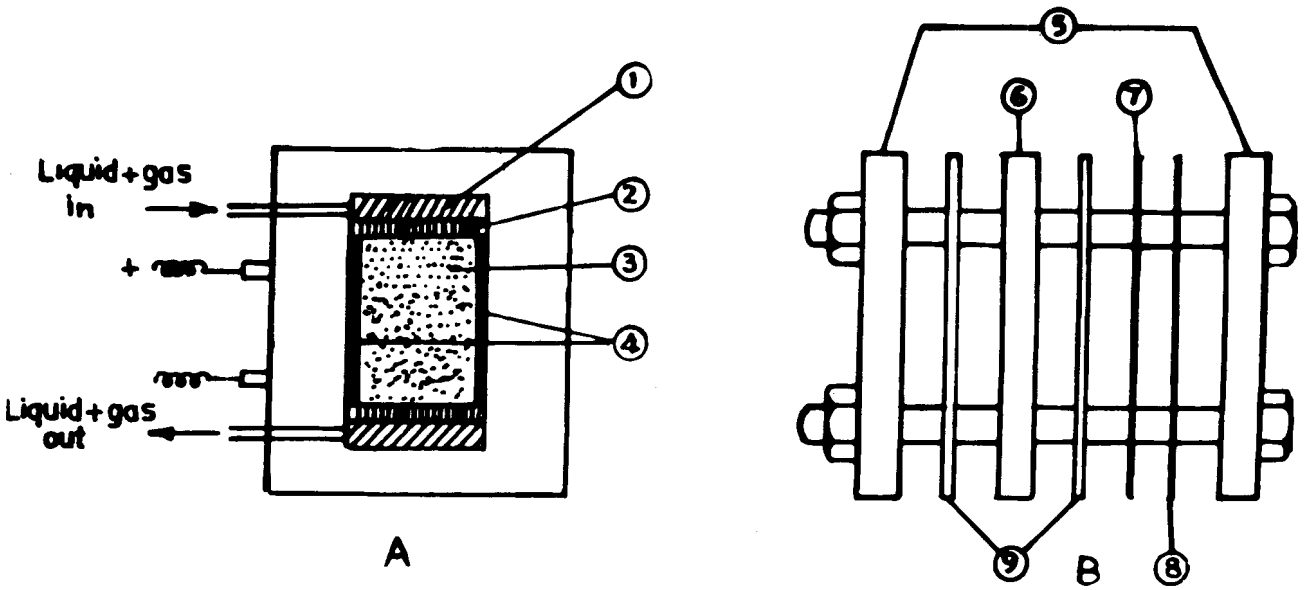

Fig.1. Trickle bed reactor; A: sectional view; B: end view
1. Glass wool
2. Distributor
3. Graphite particle bed
4. Current feeder graphite
6. PVC cell compartment
7. Nylon diaphragm
8. S.S. anode
9. Gasket

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In the present work, the preparation of sodium perborate using a trickle-bed reactor is reported after examining the conditions for oxygen reduction to get hydrogen peroxide in the same trickle-bed reactor.

EXPERIMENTAL

Trickle-bed reactor

The trickle-bed reactor consisted of a bed of graphite particles in the size ranging from -10 to +50 mesh acting as cathode and stainless steel plate acting as anode and compressed by two perspex end plates on either side. A nylon cloth in three-layers was placed between the electrodes to act as separator. While the dimensions of the cell were 25cm (l) x 15cm (w), the graphite bed occupied 10cm x 5cm (i.e.0.5 dm^2). Graphite strips placed on either side of the bed served as current feeder for the graphite particles. Rubber gaskets were placed on either side of the cathode compartment. The entire assembly was bolted together to form a leak-proof cell. The schematic diagram of the cell is shown in Fig.1.

Electrolysis

Oxygen gas was supplied from a cylinder whose pressure was regulated by means of a gas regulator and the flow rate was maintained constant with the help of a monometer. The oxygen was allowed to mix with the sodium hydroxide solution in a T-arrangement before entering the reactor. Direct current was supplied from a rectifier (0-25V; 25A). The solution was circulated continuously either by means of a pump or by gravity. The flow rates of oxygen and sodium hydroxide solution were maintained constant.

The experiments were carried out varying the current density, flow rate and concentration of sodium hydroxide to study their effects on current efficiency for the formation of hydrogen peroxide. Further experiments were conducted at the optimised conditions with the addition of borax to the electrolyte.

Analysis

The solution after electrolysis was analysed by permanganametry [10].

RESULTS AND DISCUSSION

The results on the formation of hydrogen peroxide are shown in Tables I to III, while Tables IV and V give the results with the addition of borax to the electrolyte.

H_2O_2 formation

The effect of current density on the formation of H_2O_2 is shown in Table I and the results indicate that lower current densities favour to get higher efficiency of H_2O_2 .

TABLE-I: Variation of current density on the formation of H_2O_2

Electrolyte: NaOH (1.5M); Gravity flow; (Flow rate: 6.4 to 6.9 l/hr); Temperature: 307-309K; Volume: 4 l

S.No.	Current (A)	Voltage (V)	Current density (kA. m^{-2})	Total quantity of electricty (A. hr)	Current efficiency (%)
1.	0.5	1.8	0.1	1	35.7
2.	1	1.8	0.2	2	9.4
3.	4	2.8	0.8	8	0.6

When the variation of flow rate is studied, it is found that current efficiency increases with the increase of flow rate (vide Table II).

TABLE-II: Variation of liquid flow rate on the formation of H_2O_2
Electrolyte: NaOH (1.5M); Current density = 0.1kA. m^{-2}; Current = 0.5A
Total quantity of electricity : 1 Ahr; Temperature: 307K

S. No.	Flow rate of electrolyte (l/hr)	Voltage (V)	Current efficiency (%)	Volume of electrolyte (l)	Remarks
1.	6.36	1.8	35.7	4	Gravity flow
2.	11.1	1.4	39.3	4	-do-
3.	14.4	1.2	55.2	2	Pumped flow

As the concentration of NaOH decreases, the current efficiency for the formation of H_2O_2 increases as revealed by the results of Table III.

TABLE-III: Variation of concentration of NaOH on the formation of H_2O_2
Flow rate: 13.8-15.6 l/hr (other conditions as in Table II)

Sl.No	Concentration of NaOH (M)	Voltage (V)	Current efficiency (%)
1	0.5	1.5	86.9
2	1	1.3	78.9
3	1.5	1.2	55.2
4	2	1.3	47.9

The main reactions involving formation, reduction and oxidation of perhydroxyl ion are:

$$O_2 + H_2O + 2e \longrightarrow HO_2^- + OH^- \quad \ldots (1)$$

$$H_2^- + H_2O + 2e \longrightarrow 3OH^- \quad \ldots (2)$$

$$HO_2^- + OH^- \longrightarrow O_2 + H_2O + 2e \quad \ldots (3)$$

This complex process is dependent on the interaction of liquid and gas flow rate, current density, temperature, cathode material and its particle size and electrolyte composition.

Based on the above reactions, some of the observations of Tables I to III can be explained. At higher current densities, it is probable that the reduction of perhydroxyl ion is favoured [5] and hence lowering of current efficiency for the formation of H_2O_2. When the flow rate of the electrolyte is higher, it is expected that H_2O_2 formed is removed faster from the zone of reaction (and hence its concentration reduced) and thereby avoiding the reactions (2) and (3) as well as self-decomposition of H_2O_2 which are responsible for loss of peroxide [6].

The decreasing current efficiency with increasing concentration of NaOH is due to anodic oxidation of HO_2^- being favoured by the higher OH^- concentration. The auto-decomposition of H_2O_2 is also favoured at higher alkalinity, resulting in lower efficiency.

Sodium perborate formation

Under optimum conditions arrived at for H_2O_2 formation (as described above), borax was added to the electrolyte along with 1 g/l magnesium silicate prepared by double decomposition of soluble sodium silicate with magnesium chloride. This also amounted to the presence of sodium chloride obtained during double decomposition reaction. The results are shown in Table IV, where the current efficiency had increased almost nearing quantitative formation.

TABLE-IV: Effect of addition of borax to the electrolyte
Concentration of NaOH: 1M; Magnesium silicate: 1g/l
Sodium chloride: 1 g/l (other conditions same as in Table III)

Sl.No	Borax (g/l)	Voltage (V)	Temperature (K)	Current efficiency (%)
1	0	1.3	308-313	78.9
2	30	1.3	311-313	98.7
3	40	1.3	312-315	96.7

The increase in current efficiency may be attributed to the fixing up of the unstable H_2O_2 formed with metaborate ion to form perborate as follows:

$$BO_2^- + H_2O_2 \longrightarrow (BO_2 . H_2O_2)^- \quad \ldots (4)$$

As the insoluble magnesium silicate tended to clog the bed, soluble sodium silicate was used in other experiments. The results in Table V indicate that current efficiency lowers with increase of current density, as has already been observed with the formation of H_2O_2.

TABLE-V: Variation of current density at high flow rate of electrolyte (14.4 l/hr)
Solution composition: NaOH: 1M; Borax : 30 g/l, NaCl : 1 g/l; Na_2SiO_3: 2g/l

Sl.No.	Current Density ($kA.m^{-2}$)	Voltage (V)	Temperature (K)	Current efficiency (%)
1	0.1	1.3	310-315	90.8
2	0.2	1.6	309-312	46.8

However to arrive at a commercially viable process, more detailed studies on other parameters like gas flow rate, particle size etc. are to be made.

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