In-situ Production of Hydrogen Peroxide in an Ion-exchange Membrane Cell

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Abstract—**Hydrogen peroxide is one of the most important chemicals used in pulp bleaching because of environmental restrictions on the use of chlorine based bleaches. Utmost care has to be exercised in the production, storage and transportation of Hydrogen peroxide, as it is decomposed by even minute amounts of catalytic impurities. In view of the above, in-situ production of hydrogen peroxide is gradually gaining ground. For the in-situ production of hydrogen peroxide, electro reduction of oxygen at porous cathodes is more suited. Performance data of an ion exchange membrane electrolyser for hydrogen peroxide production is reported**

Index Terms— **Hydrogen peroxide, Ion-exchange membrane cell, In-situ production.**

I. INTRODUCTION

Hydrogen peroxide is one of the most important chemicals used in pulp bleaching because of environmental restrictions on the use of chlorine based bleaches [1]. It is used in textile industry for the bleaching of fibers. Hydrogen peroxide is increasingly used in environmental protection to detoxify effluents containing formaldehyde, phenol or cyanide and deodorize sulfur containing effluents. It is used in the preparation of other peroxide compounds. In organic chemical industry, hydrogen peroxide finds extensive application as a nonpolluting oxidizing agent. Ultra pure hydrogen peroxide is used as a cleaning agent to remove organic materials, metallic impurities and particles during microchip production process. Hydrogen peroxide is also used as a propellant in space technology.

In India, demand for hydrogen peroxide has nearly doubled between 1985 and 2000. In view of the recent restriction on the usage of chlorine for the bleaching of pulp and textiles, demand is expected to increase substantially [2]. During 2000, 28122 tonnes of hydrogen peroxide was produced and 33 586 tonnes was imported. In other words more than 50 % of the demand was met by imports.

Hydrogen peroxide has been manufactured by the processes based on the reaction of sodium or barium peroxide with mineral acids, electrolysis of sulphuric acid or sulphates, auto oxidation of alkyl anthraquinone, isopropanol or hydrazobenzene and more recently by the cathodic reduction of oxygen. Utmost care has to be exercised in the production,

storage and transportation of hydrogen peroxide, as it is decomposed by even minute amounts of catalytic impurities. In view of the above, in-situ production of hydrogen peroxide is gradually gaining ground. In the present paper, an ion exchange membrane cell process involving reduction of oxygen at porous cathodes is proposed for in-situ production of hydrogen peroxide and results of the process optimization studies are reported.

II. EXPERIMENTAL METHODS

1) Cell Components

A sheet of acrylic polymer is cut into two blocks of dimension 2 cm × 12 cm × 12 cm. In each block a cavity of dimension 1.5 cm × 10 cm × 10 cm is machined at the centre. These blocks serve as anode and cathode compartments.

Titanium substrate insoluble anode (TSIA) with expanded titanium mesh configuration is used as anode. Catalytic coating of IrO_2 (45%) + TiO_2(55%) of film thickness 7µm is developed on pretreated Ti substrate by thermal decomposition technique [3]. Coating is built up by layer by layer by brushing mixed solutions of $IrCl_3$ and $TiCl_4$ in isopropyl alcohol on the substrate and thermally decomposing in a pre heated furnace at 450°C. Dimensions of the anode are 2-3 mm larger than that of the cavity. Anode is flush mounted to the matching groove machined at the periphery of the cavity. The edges of the anode are sealed using an epoxy based adhesive. A strip, which is an integral part of the anode base extend outside the anode compartment for giving electrical connections.

Perforated stainless steel sheet of dimensions 2–3 mm lesser than that of the cavity serves as the cathode current collector. It is pressed in to the cavity and held in position by applying epoxy based adhesive. This also has a strip which is an integral part of the base extend out side the cathode compartment for giving electrical connection. Layers of graphite felt are used as porous cathode. The dimensions of the felt are almost the same as the cavity. They are stacked one over the other on the current collector to fill the entire cavity.

The anode compartment has an electrolyte inlet at the bottom and an outlet at the top. The cathode compartment has an electrolyte inlet and oxygen gas inlet at the top and a common outlet for electrolyte and unreacted oxygen at the bottom. Outlet diameter is larger than inlet diameter to accommodate the two phase flow at the outlet.

2) Cell Assembly

The electrolyte compartments are arranged in such a way that the anolyte and catholyte flows are counter current
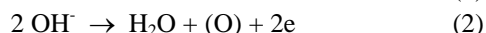
to each other. Nafion® 117 membrane acts as separator between the two compartments. 3 mm thick EPDM gaskets are placed between the compartments and membrane. The cell stack is held together by means of mild steel back plates and tie rods. The cell so assembled is made leak proof by the proper tightening of the tie rods.
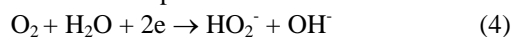
3) Equipments

A 40V 25A silicon diode rectifier is used for passing electric current to the electrolyser. Cell current and cell voltage are measured using 3½ digit digital ammeter and 3½ digit digital voltmeter respectively. Oxygen gas feed rate to the cell is measured using a gas flow meter. The electrolyte flow rate to the cell is monitored using peristaltic pumps.

4) Principle of membrane cell process

10wt % caustic solution is fed from the bottom of the anode compartment. 5wt % caustic solution and oxygen gas are fed from the top of the cathode compartment. When dc current is passed, oxygen gas is evolved at the anode and sodium ions are transported across the membrane to the cathode compartment. Anolyte gets depleted in caustic and lean caustic flows out of the anode chamber along with oxygen gas.

$$NaOH \Leftrightarrow Na^+ + OH^- \qquad (1)$$
$$2\,OH^- \rightarrow H_2O + (O) + 2e \qquad (2)$$
$$2\,(O) \rightarrow O_2 \qquad (3)$$

At the cathode, hydroxyl and peroxide ions are generated by the reduction of oxygen. Hydroxyl ions combine with the sodium ions transported from anode compartment to form caustic. Concentrated caustic and hydrogen peroxide flow out of the cathode compartment.

$$O_2 + H_2O + 2e \rightarrow HO_2^- + OH^- \qquad (4)$$
$$Na^+ + OH^- \rightarrow NaOH \qquad cf\ (1)$$

Theoretically one mole of hydrogen peroxide is produced for every two faraday of current passed. The Principle of membrane cell is illustrated in Fig.1
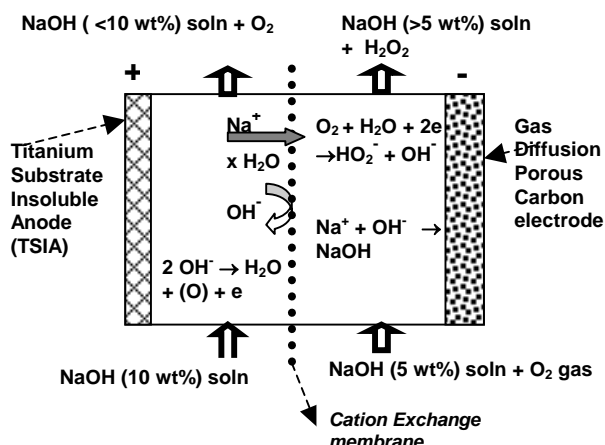

NaOH (<10 wt%) soln + O₂   NaOH (>5 wt%) soln + H₂O₂

Fig.1: Principle of membrane cell for H_2O_2 synthesis

The Parameters involved in the performance evaluation of the any electrolytic process are current density, current efficiency and specific power consumption. So electrolysis

was carried out at different current densities by the constant current method. Cell voltage and concentration of hydrogen peroxide produced are monitored. Concentration of hydrogen peroxide produced was determined by the permanganate titration method [4]. Current efficiency of the process and specific power consumption are calculated. One drawback of porous cathodes is low gas utilization efficiency [5]. Theoretical oxygen requirement for this process is only 0.47 litre at STP per Ampere hour current passed. Effect of oxygen flow rate on the concentration of hydrogen peroxide formed and current efficiency are also studied. Addition of EDTA to the anolyte has been reported to increase current efficiency and to prevent fouling of the membrane [6]. So effect of EDTA dosage was also studied.

III. RESULTS AND DISCUSSION

The combination of trickle bed cathode and cation exchange membrane in a two compartment cell solves most of the problems associated with limiting oxygen mass transport. Enhanced oxygen mass transfer is achieved because the cathode reaction occurs in a co-stream of catholyte and oxygen gas on the porous carbon felt cathode. Further both the electrolyte and oxygen gas are fed from the top of the compartment. This most probably leads to more or less uniform dispersion on the porous cathode resulting in the prevention of decline in current efficiency. Further the cation exchange membrane prevents the back migration of the anion, thereby resulting in improved current efficiency.

Production cost consists of operating cost and fixed cost. The operating cost includes the power cost, cost of EDTA and cost of oxygen gas. The raw materials are readily available everywhere. Except power cost, the cost the rest is more or les the same at all locations. Cost of power varies from location to location. NaOH solution used as anolyte and catholyte is available in plenty in all paper and pulp mills. Therefore cost of NaOH is not included in the operating cost.

1) Effect of current density

With increase in current density, increase in concentration of hydrogen peroxide produced is marginal. Concentration of hydrogen peroxide produced is around 0.7 M. Current efficiency decreases and terminal voltage increases with increase in current density as shown in Fig 2 and Fig 3. Therefore electrical power consumption increases with increase in current density. Hence operating cost is the lowest at the lowest current density. On the other hand, higher current density is desired to reduce total area of the anode producing the required volume of Hydrogen peroxide.
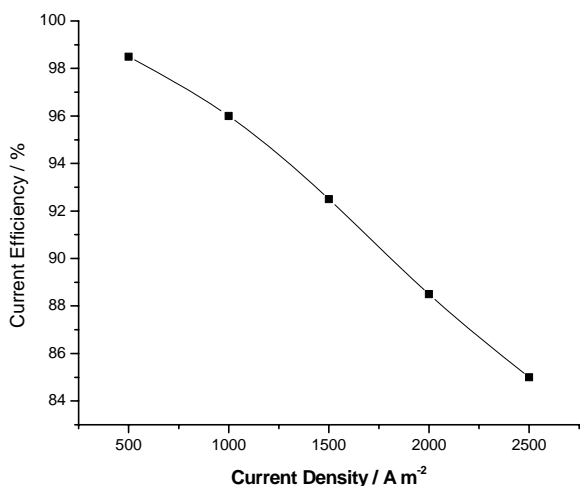
Fig. 2. Effect of Current density on current efficiency for H_2O_2 synthesis
Anolyte concn. : 10 wt%; EDTA dosage : 200 ppm;
Catholyte concn.: 5 wt%; O_2 supply : 20 times theoretical; Temperature : 303 K
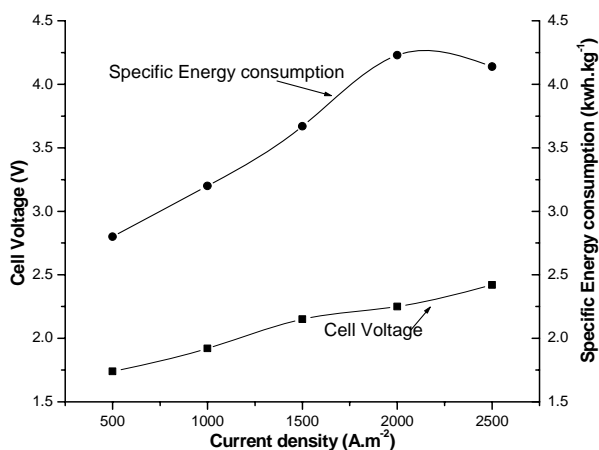

Fig. 3. Influence of Current density on Cell voltage and Specific energy consumption for H_2O_2 synthesis.
Anolyte concn. : 10 wt%; EDTA dosage : 200

Production cost, which is the sum of fixed cost and operating cost, depends to a large extent on the local electric power cost. For locations, where power cost is minimum, $2500A \ m^{-2}$ current density is optimum. At locations where power cost is maximum, $1000A \ m^{-2}$ is the optimum current density.

2) Effect of EDTA dosage
Ethylene diamine tetra acetic acid salt (EDTA) is added to the anolyte in order to prevent fouling of the ion exchange membrane during electrolysis. Major cost of production is the plant cost. Plant cost is lowest at the maximum current density. So the effect of EDTA dosage was studied at the maximum current density of $2500A.m^{-2}$. Current efficiency increases and electric power consumption decreases with increasing EDTA dosage. Results are tabulated in Table 1.

Table 1. Effect of EDTA dosage

EDTA Dosage (ppm)	Current Efficiency (%)	Specific Energy Consumption (kWh.kg^{-1})
50	75	4.70
100	78	4.52
150	82	4.30
200	85	4.14
250	85	4.14

Note:
Anolyte concn: 10 wt%.,Current density : $2500A.m^{-2}$
Catholyte concn.:5 wt%, O_2 supply :20 times theoretical, Temperature: 303 K

Current efficiency is maximum and specific energy consumption is minimum at above an EDTA dosage of 200 ppm. On the other hand with increase in EDTA dosage EDTA cost also increases, increasing operating cost. The minimum EDTA dosage at which specific energy consumption is the least is the optimum EDTA dosage, which is 200 ppm.

3) Effect of oxygen supply ratio
Oxygen supply ratio is defined as the ratio of the volume of the actual oxygen supplied to the theoretical requirement for any current density. Theoretical oxygen requirement for this process is only 0.47 litre at STP per Ampere hour current passed. As the oxygen supply cost (operating cost of the oxygen blower) is one among the operating costs. So the oxygen supply ratio should be very close to one, for the process to be commercial viable. But when stoichiometric amount of oxygen is passed current efficiency is as low as 35%. As the oxygen supply ratio is increased current efficiency also increases. Effect of oxygen supply ratio on the cost of production was also studied at the maximum current density $2500 \ A.m^{-2}$ for the reasons discussed earlier. The results are shown in Table 2.

Table 2. Effect of oxygen supply ratio

Oxygen Supply Ratio	Current Efficiency (%)	Specific Energy Consumption (kWh.kg^{-1})
5	55	6.40
10	71	5.02
15	80	4.40
20	85	4.14
25	85	4.14

Note: Anolyte concn .: 10 wt%.,Current density: 2500 $A.m^{-2}$, Catholyte concn.: 5 wt%, O_2 supply : 20 times theoretical, temperature: 303 K

Current efficiency is maximum and specific energy consumption is minimum at above an oxygen supply ratio of 20. On the other hand with increase in oxygen supply ratio, oxygen cost also increases, increasing operating cost. The minimum oxygen supply ratio at which specific energy consumption is the least is the optimum oxygen supply ratio, which is 20.

IV. CONCLUSION

An ion exchange membrane cell process involving reduction of oxygen at porous cathodes is proposed for in-situ production of hydrogen peroxide and the vital process parameters have been optimized.

The optimized parameters are:

Current density   : $2500 \ A \cdot m^{-2}$.
Anolyte concentration   :   10 wt% NaOH
Catholyte concentration :   5 wt% NaOH
EDTA dosage   :   200 ppm
Oxygen supply ratio   :   20

When the cell is operated under the optimized conditions, specific power consumption is $4.14 \ kWh \cdot kg^{-1}$ of H_2O_2.

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