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Hydrogen peroxide production in trickle-bed electrochemical reactors

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A trickle bed electrochemical reactor has been developed for the production of dilute alkaline peroxide solutions by reduction of oxygen. Oxygen gas and sodium hydroxide flow concurrently downward through a cell which consists of a thin packed cathode bed of graphite particles separated from the anode plate by a porous diphragm. Current flows perpendicular to the flow of electrolyte. The effects of current density, oxygen pressure and flow rate, electrolyte concentration and flow rate, graphite particle size, bed thickness and length were investigated. In 2 M NaOH peroxide solutions of 0·8 M have been produced at 60% efficiency with current densities of 1200 A m^{-2} and cell voltages of 1·8 V. A bipolar cell stack consisting of five cells has been tested.

1. Introduction

Dilute alkaline peroxide solutions have been prepared by the electroreduction of oxygen in fixed- and fluidized-bed cathodes operated in two- and three-phase flow modes in divided membrane cells [1, 2]. The highest peroxide concentrations, current and power efficiencies were obtained with oxygen gas and alkaline electrolyte flowing concurrently downward through a fixed bed of graphite particles in the manner of a trickle bed catalytic chemical reactor. Concentrations of peroxide sufficiently high for use in bleaching (0·15 M) were made under oxygen pressures of 800 kPa. However voltage drops were high and current densities were low. For industrial purposes a pressurized packed-bed cell divided by a membrane and with separate anolyte and catholyte flows suffers from several disadvantages. Subsequent work reported here has been directed towards the development and characterization of a simpler undivided cell which uses a porous diaphragm rather than an ion exchange membrane and thus dispenses with the need for separate anolyte and catholyte circulation systems [3].

2. Experimental

The trickle-bed electrochemical reactor developed in this work consisted of a metal cathode plate, a thin bed of graphite particles, a porous nonconducting diaphragm and a metal anode plate compressed in a sandwich as shown in Fig. 1. The graphite beds were contained in asbestos/neoprene gaskets and the electrode plates held between bolted mild steel channels to hold internal pressures of up to 2000 kPa. Dimensions of three reactors used are given in Table 1. A variety of electrode plate and diaphragm materials have been used, but the present results are confined to the use of stainless steel electrode plates, and nylon or polypropylene diaphragms. Under conditions reported here, there was a little corrosion of the anode, but this was not a serious problem.

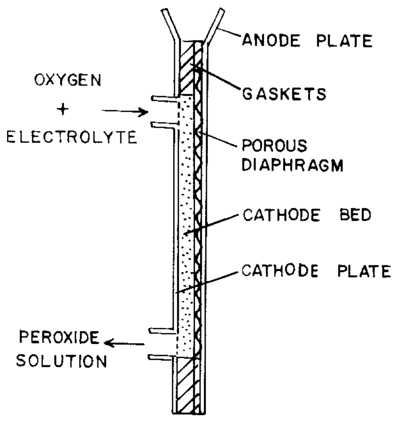

Fig. 1. Trickle bed electrochemical cell.

Table 1. Dimensions of trickle bed cells used

bed width	50 mm
bed thickness	1·5–6 mm
bed length	0·5, 0·78, 2 m
graphite particle size (average)	0·3–1·0 mm

The reactor is operated with concurrent flow of oxygen gas and NaOH electrolyte downward through the graphite bed. Current is fed to the cell through the protruding ends of the metal electrode plates and flows perpendicular to the direction of liquid and gas flow. A simplified diagram of the cell and its auxiliary flow and control system is shown in Fig. 2. For tests on the largest cell a 1000 A power supply was used.

Experimental runs involved pumping a premixed stream of oxygen and sodium hydroxide solution into the reactor, while supplying power to the electrodes with the power supply in the controlled current mode. Samples of the product solution were taken at steady state and a record made of the electrolyte flow, oxygen flow, cell current and voltage, product temperature and pressure at the cell inlet and outlet. The peroxide concentration in the product was determined by titrating an acidified 1 ml aliquot with 0·02 M potassium permanganate solution.

The electrolyte solution was made up using commercial grade sodium hydroxide and deionized tap water unless otherwise indicated. Compressed oxygen gas was 99·5% O_2 obtained from Canadian Liquid Air in standard cylinders.

3. Discussion of results

The reduction of oxygen to peroxide in a trickle bed cell is a complex process whose efficiency depends on an interaction of many important variables. The main chemical reactions involving formation, reduction and oxidation of perhydroxyl ion are

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

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad (2)$$

$$HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e^-. \qquad (3)$$

The balance of the formation and reduction reactions depends primarily on the cathode material [4] and to a lesser extent on the oxygen pressure, peroxide concentration and effectiveness of mass transfer [5]. The reduction reaction is relatively slow on graphite but becomes important at oxygen pressures around 1000 kPa when the perhydroxyl concentration approaches 1 M. The effects of these factors are moderated by the electrode potential distribution through the bed in

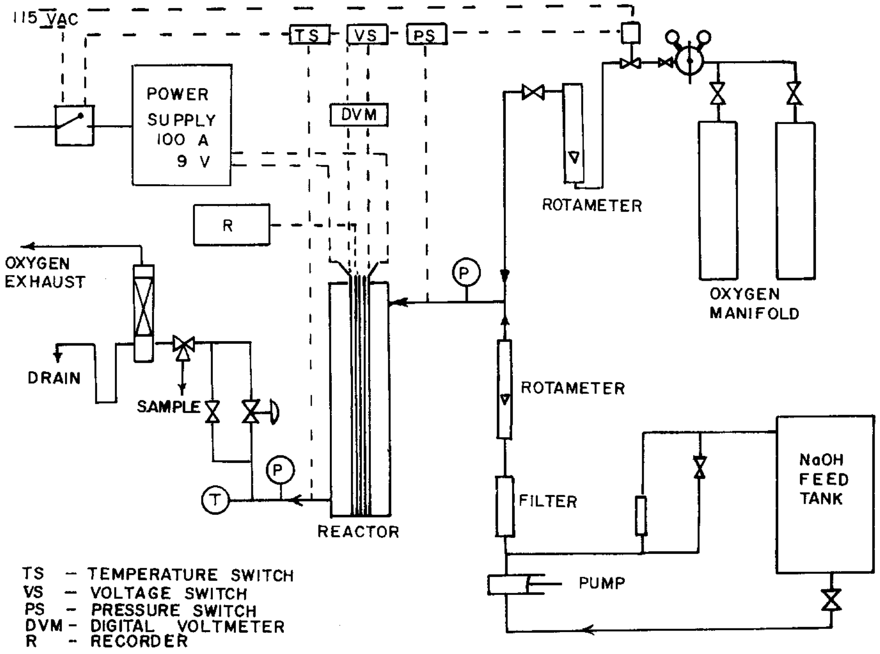

Fig. 2. Process flow and control schematic.

the direction of the current [6]. Due to ohmic losses in the electrolyte the cathode potential is a maximum nearest the counter-electrode and falls toward the cathode feeder. Under favourable conditions the electro-active bed thickness can be of the order of 10 mm [7] but this is lowered with decreasing conductivity or hold-up of the electrolyte. Increasing local rates of electrode reaction also compresses the electro-active zone, as may result from higher reactant concentration, enhanced mass transfer or increased specific area of the catalyst particles. With other things equal higher superficial current densities can extend the effectiveness of the bed at the expense of increased electrode potentials, which may promote secondary reactions.

Loss of peroxide due to anodic oxidation depends on diaphragm thickness and permeability, current density and hydroxyl concentration. Both hydroxyl and perhydroxyl ions are transported through the diaphragm to compete for anode reactions. The oxidation reaction is quite fast and most perhydroxyl ion reaching the anode is probably destroyed. The main anodic reaction is the generation of oxygen from hydroxyl ions.

Performance of such a cell would be expected to depend on fluid mechanical and geometric parameters as well as the rates of the above reactions. The nature of the flow through the cell will influence mass transfer, cell resistance and conversion efficiency. Although most work on trickle bed chemical reactors is done using cylindrical reactor vessels rather than the thin rectangular cells described in this work some preliminary comparisons may be made. According to a diagram of Satterfield [8] the flow in a trickle bed electrochemical cell should be in the gas-continuous regime at the flow rates used in the present work. Visual observation at atmospheric pressure indicated that the liquid was in trickling flow and the gas phase was continuous. Voltage drop in the cell is not prohibitive however. Geometrical considerations [10] suggest that the trickle bed cell would operate in near plug flow. Flow characteristics in trickle bed electrochemical cells including axial dispersion measurements will be reported in a subsequent paper.

The influence of major operating and design variables on the current efficiency, peroxide yield and voltage requirements in the trickle bed cell have been studied. The results of these experiments are summarized below.

3.1. *Superficial current density*

Fig. 3 illustrates the results of the effect of superficial current density (i.e. current density based on the area of the metal cathode current feeder plate) at fixed values of liquid and gas flow rate and cell pressure. The concentration of peroxide in the cell exit liquor from the 0·5 m long cell approaches an asymptotic value of about 0·7 M as the current density approaches 1500 A m^{-2}. The voltage drop across the cell increases in an almost linear fashion with current density, reaching a value of 2·6 V at 1500 A m^{-2}. Current efficiency decreases from 84% at 500 A m^{-2} to 60% at 1500 A m^{-2}.

These typical results indicate that useful concentrations of peroxide can be made in a trickle bed cell without a membrane. In the undivided cell some oxidation of peroxide was expected, but the amount of peroxide loss appears limited, particularly at current densities below 1000 A m^{-2}. The trickle bed diaphragm cell then represents a major simplification in cell design and process hardware over the divided membrane cell. Compared to previously reported results [2] which used an 0·1 M NaOH catholyte in a divided cell with anode

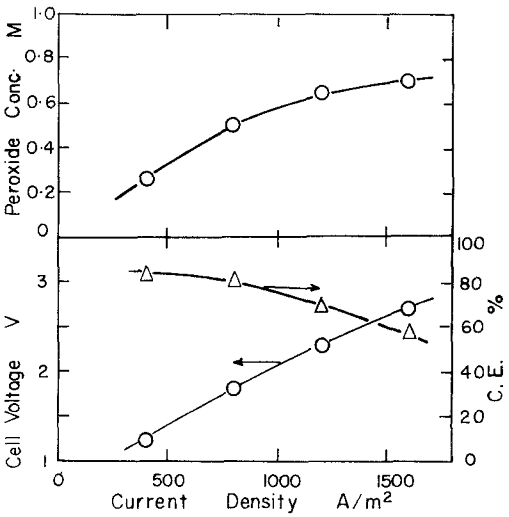

Fig. 3. Effect of current density on peroxide concentration, cell voltage and current efficiency. Temperature 298–313 K; electrolyte 2 M NaOH; pressure 930 kPa; liquid rate 10^{-5} m^3 min^{-1}; cell area 0·025 m^2; gas rate $1{\cdot}9 \times 10^{-3}$ m^3 min^{-1}; graphite size $-$ 0·42 + 0·30 mm; bed thickness 3 mm.

and cathode chambers each 7 mm thick and separated by a cation membrane, the voltage drop has been reduced from 10–15 V to about 2·5 V. At the same time the peroxide concentration was increased from about 0·15–0·7 M with superficial current densities a factor of two to three higher and at considerably higher current efficiencies. Part of this improvement is due to the increased concentration of NaOH used in the cell.

3.2. *Oxygen pressure*

The role of oxygen pressure is seen in Fig. 4. Current efficiency increases from about 56–71% at 1000 A m^{-2} as the outlet oxygen pressure is increased from 450–1140 kPa. Peroxide concentration increases from 0·64–0·85 M at the same current density. The increase in peroxide concentration is far from proportional to the increase in oxygen pressure. At 790 kPa, increasing the oxygen pressure by a further 43% raises the peroxide concentration from 0·78–0·85 M. The positive effect of pressure on oxygen solubility is moderated by secondary electrode reactions whose rates increase with peroxide concentration. No significant change in cell voltage with oxygen pressure is apparent but other results show a drop of 0·1 V at 1000 A m^{-2} when pressure is raised from 790–1580 kPa. Pressure drop varies with operating conditions and is generally in the range 20–120 kPa m^{-1}. Some other data on pressure effects are discussed below.

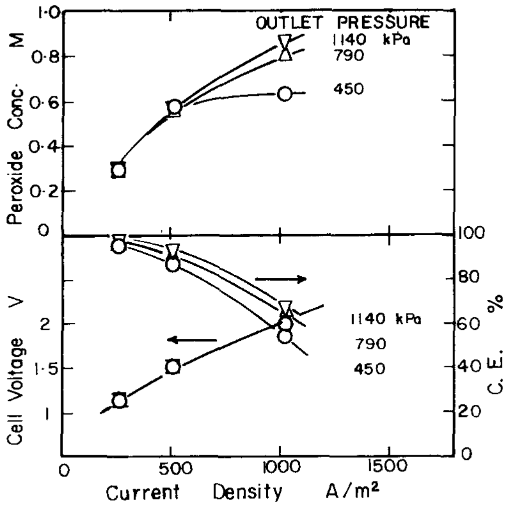

Fig. 4. Effect of outlet oxygen pressure on peroxide concentration, cell voltage and current efficiency. Temperature 295–308 K; electrolyte 2 M NaOH; cell area 0·039 m^2; liquid rate $1{\cdot}05 \times 10^{-5}$ m^3 min^{-1}; graphite size − 0·42 + 0·35 mm; gas rate $1{\cdot}9 \times 10^{-3}$ m^3 min^{-1}; bed thickness 3 mm.

3.3. *Graphite particle size and cathode bed thickness*

Two size cuts of graphite particle were tested in the 0·78 m long reactor, each at three different cathode bed thicknesses and two outlet oxygen pressures. The results are listed in Table 2. At a superficial current density of 1025 A m^{-2} peroxide concentrations of about 0·8 M are obtained in 2 M sodium hydroxide with current efficiencies around 50%. In general an increase in bed thickness from 1·5–3 mm raises the current efficiency, but a further increase of the thickness to 6 mm gives no significant improvement. The effect of bed thickness is less important at the higher oxygen pressure of 1620 kPa, probably because the higher reaction rates drive the electro-active zone nearer the anode. Decreasing the average graphite particle size from 0·5–0·2 mm at fixed oxygen pressure has no significant effect on efficiency at 810 kPa but a small negative effect at 1630 kPa. This result is contrary to expectations with the higher surface area and mass transfer rates of smaller particles. However a full interpretation of these numbers is complicated by the fact that the graphite particles are porous with a specific surface of the order of 1 m^2 g^{-1} which is nearly independent of particle size and by the effect of decreased particle size on the non-idealities of the process, such as increased pressure drop (from about 30 kPa to 60 kPa) and by-passing of electrolyte through the porous diaphragm.

3.4. *Reactor length and flow rate of gas and liquid*

The effects of reactor length and flowrate at fixed current density are shown in Fig. 5[*]. Experiments were carried out in the 2 m long cell which is equipped with sample taps at different positions. Data for a 4 m length were obtained by using two beds side by side in the 2 m cell. Electrolyte and oxygen flowed through each bed in series. The peroxide concentration does not increase proportion-

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[*] All oxygen flows are referred to STP.

Table 2. Effect of graphite particle size and cathode thickness (cell size 0·050 m × 0·78 m; oxygen flow $2 \times 10^{-3}\,m^3\,min^{-1}$; current density $1025\,A\,m^{-2}$; 2 M NaOH flow 7–8·5 × $10^{-6}\,m^3\,min^{-1}$; temperature 303 K)

Graphite size (mm)	*Outlet pressure* (kPa)	*Current efficiency* (%)	H_2O_2 (M)	*Cathode thickness* (mm)
– 0·60 + 0·42	811	41	0·61	1·5
– 0·60 + 0·42	811	52	0·80	3
– 0·60 + 0·42	811	53	0·75	6
– 0·60 + 0·42	1622	50	0·83	1·5
– 0·60 + 0·42	1622	59	1·05	3
– 0·60 + 0·42	1622	51	0·85	6
– 0·30 + 0·09	811	34	0·71	1·5
– 0·30 + 0·09	811	57	0·84	3
– 0·30 + 0·09	811	54	0·84	6
– 0·30 + 0·09	1622	46	0·77	1·5
– 0·30 + 0·09	1622	47	0·84	3
– 0·30 + 0·09	1622	48	0·86	6

ately with reactor length due to several interacting factors. As the concentration of perhydroxyl ion increases, the rate of oxidation will increase and the rate of peroxide formation will decrease. The concentration of hydroxyl ion and the conductivity of the electrolyte will also fall with increasing electrode length.

As expected from previous work [2] the peroxide concentration increases with increasing oxygen flow rate, and decreasing liquid flow rate, with the latter being the more important parameter. Doubling the gas rate increases peroxide concentration by only about 10%, whereas a 40% reduction in liquid rate from 36 × $10^{-6}m^3min^{-1}$ to 21 × $10^{-6}m^3min^{-1}$ increases peroxide concentration by about 65%.

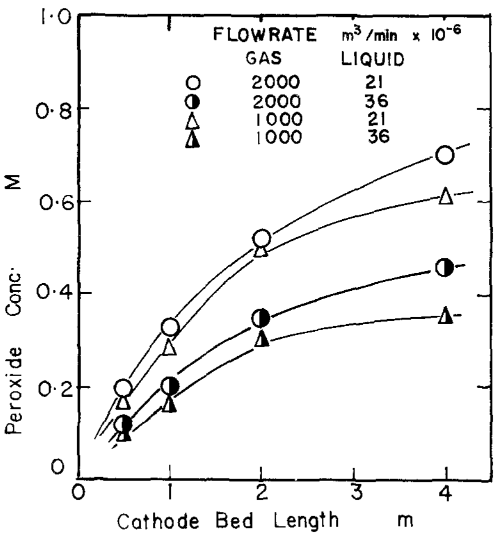

Fig. 5. Effect of cell length and flow rates on peroxide concentration. Temperature 295–300 K; graphite size – 0·99 + 0·30 mm; pressure 790 kPa; bed thickness 3 mm; cell area 0·2 m²; electrolyte 2 M NaOH; current density 500 A m⁻².

3.5. *NaOH concentration*

Higher NaOH concentrations yield higher peroxide concentrations and lower cell voltages, as shown in Fig. 6. The latter effect amounts to about 0·2 V for an increase of NaOH concentration from 1–2 M, and is mainly due to the increased electrolyte conductivity. The effect on peroxide concentration is less well understood, but may be due to several factors. The increased conductivity extends the electro-active bed thickness, and decreases the real current density on the cathode, while the preservation of perhydroxyl in the competitive anode reactions is favoured by increased hydroxyl concentration. Further, the pH of the electrolyte is decreased by the net cell reaction.

$$\tfrac{1}{2}O_2 + OH^- \rightarrow HO_2^- \qquad (4)$$

and the ionization of peroxide is depressed with decreasing pH,

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (5)$$

$$K = 2{\cdot}4 \times 10^{-12}\,\mathrm{M} \text{ at } 298\,\mathrm{K}.$$

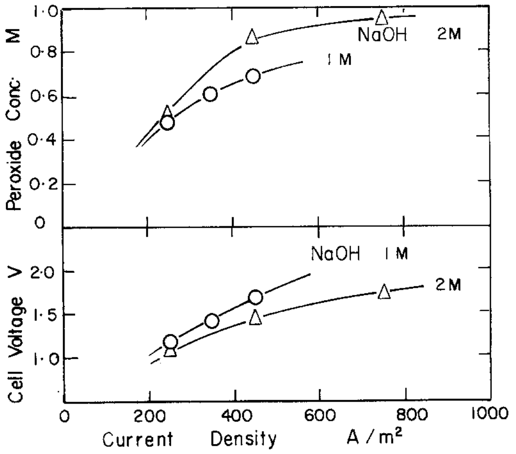

Fig. 6. Effect of electrolyte concentration on peroxide concentration and cell voltage. Temperature 298–303 K; liquid rate 1·8–2·1 $\times 10^{-5}$ m^3 min^{-1}; cell length 4 m; gas rate 2 $\times 10^{-3}$ m^3 min^{-1}; graphite size — 0·99 + 0·30 mm; pressure 1480 kPa; bed thickness 3 mm.

Since Vetter [11] suggests that the mechanism of electroreduction of peroxide is via H_2O_2, the higher initial NaOH concentration could protect the peroxide from subsequent cathode reactions. Other tests have shown that current efficiency increases with NaOH concentration from 2–4 M, but the effect is less marked than at lower concentrations.

3.6. *Adiabatic cell operation*

The effect of temperature was studied over the range of interest by operating the cell under near adiabatic conditions. This was done to simulate operation in a commercial process where only a small fraction of the electrical heat generated would be transferred from the cell stack. Under such conditions the electrolyte temperature would rise to about 350–360 K in the absence of cooling. Results of tests with an insulated cell (Fig. 7), indicate that peroxide concentration is not strongly affected at temperatures up to 350 K. Cell voltage and current efficiency decrease slightly with increasing temperature.

3.7. *Bipolar cell operation*

The geometry of the sandwich type cell lends itself readily to construction of multi-cell stacks. Tests were run in a bi-polar stack made up of five cells in series with parallel flow of gas and electrolyte as shown in Fig. 8. Results of a typical test given in Table 3 show a peroxide concentration of 0·65 M at a current efficiency of 78%. The voltage drop per cell is about 1·6 V. These results are basically comparable to those from a single cell at one-fifth the flow rate and similar current

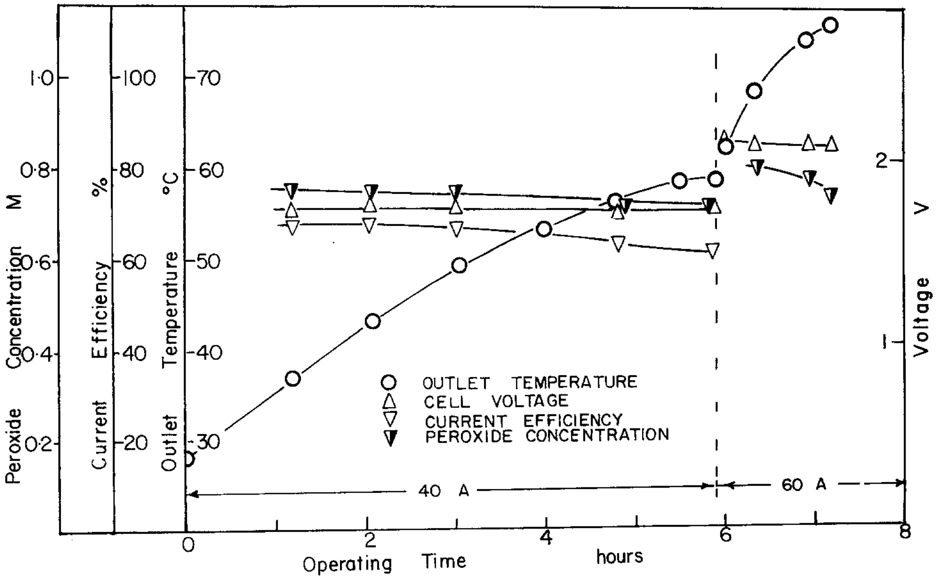

Fig. 7. Adiabatic cell operation. Bed thickness 3 mm; pressure 860 kPa; electrolyte 2 M NaOH in tap water; cell area 0·039 m^2; graphite size — 0·42 + 0·30 mm.

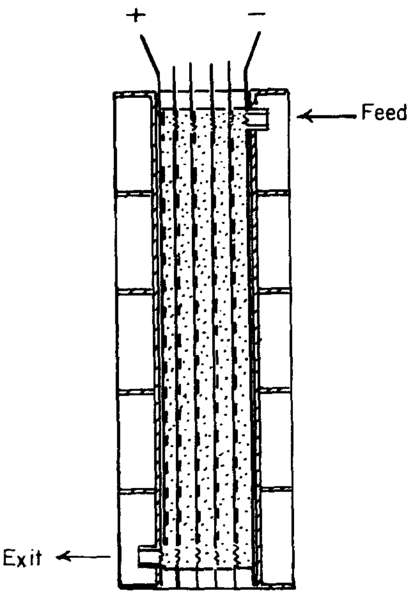

Fig. 8. Assembly of cells with bipolar electrodes.

density. This suggests that for small numbers of cells per stack, where fluid distribution problems are not severe, single cell tests may be used for scale-up to multi-cell bi-polar operation.

4. Conclusions

These studies have shown that peroxide solutions of about 0·8–1 M can be made efficiently in trickle bed diaphragm cells. With oxygen loadings of about 1 $m^3 min^{-1} m^{-2}$ and 2 M NaOH loadings of about 0·1 $m^3 min^{-1} m^{-2}$ at cell pressures of about 800 kPa current efficiencies of 60% were obtained at current densities of 1000 A m^{-2}. At lower current densities of 750 A m^{-2} a 0·65 M solution was produced at 75% current efficiency. Cell voltages of about 1·5–2 V were typical, with corresponding electrochemical energy yields of 2–7 kW h(kg H_2O_2)$^{-1}$. The effects of the main process and design variables on current efficiency and voltage drop have been elucidated and a range of suitable operating conditions determined. Operation of a bi-polar cell stack containing five cells gave promising results. The trickle bed diaphragm cell devised for this work has many advantages over the divided membrane cell used previously, and its use for peroxide production and for other processes is being explored further.

Acknowledgements

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Table 3. Bipolar cell operation

number of cells	5
size of cells	0·05 m × 0·78 m
graphite size	− 0·42 + 0·30 mm
electrolyte	2 M NaOH commercial grade in distilled water
total electrolyte flow	55 × 10^{-6} $m^3 min^{-1}$
total oxygen flow	2·5 × 10^{-3} $m^3 min^{-1}$
inlet pressure	1135 kPa
outlet pressure	720 kPa
outlet temperature	319 K
current density	770 A m^{-2}
voltage/cell	1·52–1·64
outlet H_2O_2 conc.	0·65 M
current efficiency	78%