Processes for the production of mixtures of caustic soda and hydrogen peroxide via the reduction of oxygen

P. C. FOLLER, R. T. BOMBARD

Foller and Associates, Inc., 1205 Melville Square, Unit 303, Richmond, CA 94804, USA

The long history of the synthesis of hydrogen peroxide via the cathodic reduction of oxygen in caustic soda catholyte is reviewed. Recent progress is analysed on the electrochemical syntheses of mixtures of caustic soda and hydrogen peroxide in various by-weight ratios from 2.3 : 1 NaOH to H_2O_2 to about 1 : 1. The analysis presented focuses primarily on published work concerning planar fuel cell type electrodes in membrane-divided cells and particulate bed electrodes in cells employing microporous separators with well-defined anolyte-to-catholyte flows. Potential ancillary technology for changing the ratios of products is also discussed. One configuration of the processes described encompasses the simultaneous near 50/50 use of two variations of generation technology. A highly desired product, for instance 1.2 : 1 NaOH to H_2O_2, may be formed using the catholyte product of a membrane or diaphragm cell with a caustic anolyte as the catholyte feed stream for a membrane cell with an acidic anolyte. Although the particulate bed cathode approach has reached commercial trials, the planar cathode membrane cell approach may prove a difficult process to develop as the performance of electrodes optimized for realistic hydraulic depths may prove very different to that of electrodes used in small scale laboratory development.

1. Introduction

Hydrogen peroxide has been displacing some uses of chlorine-based chemicals in the paper and pulp industry. It is being used in the bleaching of mechanical pulp, and the brightening of chemical pulp [1]. Environmental pressures on the use of chlorine chemistry are becoming increasingly severe. Concern over the discharge of chlorinated organic materials is forcing the partial conversion of bleaching sequences from chlorine and chlorine dioxide based chemistry to the use of hydrogen peroxide, oxygen, and ozone. Global hydrogen peroxide demand in pulping is growing from 190 000 mT in 1987 to a projected 514 000 mT by 1995 [2, 3]. Thus, by 1995 a \$570 million hydrogen peroxide market is forecast, at a pricing of \$1.10 kg^{-1}. Through 1994, in North America 70 wt % hydrogen peroxide traded at well below its list price of approximately \$1.50 kg^{-1} (100%) H_2O_2. It is discounted to large customers at approximately \$0.85–1.00 kg^{-1}.

Several types of hydrogen peroxide bleaching and brightening operations are performed in the presence of caustic soda [6–10]. The Kraft process, the bleaching process with the largest market share, would require concentrations of over 2–3 wt % hydrogen peroxide at ratios of 1.5–2.0 : 1 and higher [8–10]. (Concentrations of 2–3 wt % are typically applied to the pulp, although the production of higher concentrations would be desirable for process flexibility.) Uses in Kraft pulping have diminished; however,

uses in CTMP bleaching and in secondary fibre are growing. In mechanical or thermomechanical mills, the hydrogen peroxide in caustic is used on unbleached pulp at lower ratios than given above [7]. In Kraft bleaching hydrogen peroxide is used primarily in enforced alkali extraction after oxygen, elemental chlorine, or chlorine dioxide bleaching [8–10].

There are approximately 170 pulp mills in North America [11]. The average size chemical Kraft pulping facility would require 5–10 mT day^{-1} [5]. There are no CTMP mills in the United States but there are 13 in Canada [2]. These would require somewhat more hydrogen peroxide on average. Thus, a competitive on-site process might represent an attractive commercial opportunity. Small on-site electrochemical plants may be considered for supplying a base demand of hydrogen peroxide, with additions of merchant hydrogen peroxide to account for varying load and/or ratio requirements.

This communication discusses and compares several new on-site processes for the electrochemical production of mixtures of hydrogen peroxide in caustic soda that have been thought to be commercially attractive [12–69]. The particulate bed cathode approach has been evolving primarily in the patent literature for many years [55–65], and has been taken to commercial trials by Dow Chemical (Midland, MI) and H-D Tech, a joint venture of Dow and Huron Technologies, Inc. (Kingston, Ontario). The process is now being marketed by Dow [64]. Planar gas

diffusion cathode work has also been evolving for some time [22–40, 66–69]. The planar cathode work most recently reported has been performed by Prototech Company (Needham, MA) and its successor/licensee E-TEK, Inc. (Natick, MA) [12–15].

In the caustic anolyte versions of oxygen reduction processes for the generation of hydrogen peroxide in caustic soda, the chemical and electrochemical reactions are [70]:
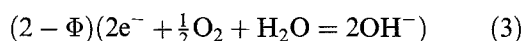
Cathode:

$$2e^- + \frac{1}{2}(1 + \Phi)O_2 + H_2O = \Phi HO_2^- + (2 - \Phi)OH^-$$ (1)
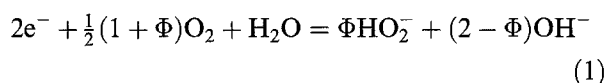
(Φ is the current efficiency for oxygen reduction.)

$$E/V = 0.338 - 0.0591\,pH$$
$$+ 0.0295\log P_{O_2}/[H_2O_2]$$ (2)
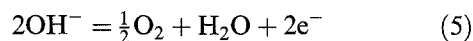
Side reaction:

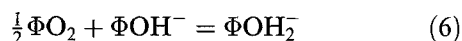$$(2 - \Phi)(2e^- + \frac{1}{2}O_2 + H_2O = 2OH^-)$$ (3)

$$E/V = 1.228 - 0.591\,pH + 0.0147\log P_{O_2}$$ (4)

(Hydrogen evolution is not observed in normal operation.)

Anode:

$$2OH^- = \frac{1}{2}O_2 + H_2O + 2e^-$$ (5)

Net reaction:

$$\frac{1}{2}\Phi O_2 + \Phi OH^- = \Phi OH_2^-$$ (6)

Which enters into the equilibrium:

$$HO_2^- + H_2O = H_2O_2 + OH^-$$ (7)
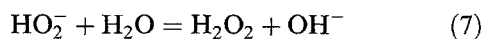
$$\log[HO_2^-]/[H_2O_2] = -11.63 + pH$$ (8)

(A diagram of the temperature dependence of this equilibrium is given in [1].)

It is possible to recirculate the anodically evolved oxygen to the cathode feed gas to provide one half of the total oxygen requirement, so, in some sense, this is a paired synthesis. Liquid ring compressor costs must be affordable, given that the Dow/H-D Tech process recycles anodic oxygen [65]. If there is a failure in the supply of oxygen, hydrogen evolution can occur. The Dow/H-D Tech process incorporates a hydrogen monitor for this reason [65].
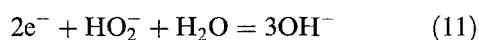
A divided cell must be used to achieve a high current efficiency because hydrogen peroxide can be electrochemically decomposed according to the following [70]:

Anodic oxidation in acid (or base):

In acid: $$H_2O_2 = O_2 + 2H^+ + 2e^-$$ (9)
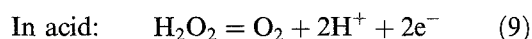
$$E/V = 1.36 - 0.295\,pH$$
$$+ 0.295\log[H_2O_2]/[OH^-]$$ (10)

Cathodic reduction in base:

$$2e^- + HO_2^- + H_2O = 3OH^-$$ (11)

$$E/V = 2.119 - 0.886\,pH + 0.0295\log[HO_2^-]$$ (12)

Chemical decomposition also occurs:

$$HO_2^- = \frac{1}{2}O_2 + OH^-$$ (13)

Because the product formed in the catholyte is to be built up to as high a concentration as is practical, the flow rate of the catholyte is very low. This means that the product has a substantial residence time within the cell. Thus, to divide anolyte and catholyte, membranes, rather than microporous separators, are, in principle, preferred in the absence of anolyte-to-catholyte flow. Any material used for dividing the cells must have oxidation resistance due to the high concentration of hydrogen peroxide.

It has been known since the 1880s that hydrogen peroxide may be formed in sodium hydroxide by the cathodic reduction of air or oxygen at high surface area carbon electrodes [17], and in the 1930s a number of US Patents were taken out on porous carbon bed structures by Berl [18, 19]. Similar work was performed in Japan [20, 21].

Carbon has been the electrode material of choice. However, other materials (such as gold) have been evaluated for their capabilities to reduce oxygen to H_2O_2 [22, 23]. ([22] shows the use of a hydrogen anode.)

Comprehensive investigations of fuel cell type electrodes were performed by a group of Czech workers [24–32]. The properties of various types of as-received carbonaceous materials were explored [24]. A mathematical model of peroxide formation and diffusion was derived [25]. Polyethylene was used as a binder, and the effect of various PE contents were studied [26]. The solubility of sodium peroxide in caustic was studied [27, 28]. Modification techniques were employed to alter the carbon surface [30]. A theory of the reactivity of various carbonaceous materials was put forward which correlated higher initial current efficiency to lower initial numbers of 'paramagnetic centres', meaning oxygen-containing surface functionality [30]. As increasing functionality accumulates over time, the hydrogen-reduced carbon surfaces favoured by this theory cannot be maintained in practice. This excellent body of work also evaluated fluorocarbon binders and used various nickel substrates.

Nickel mesh, 'nets', and gauze have also been mentioned in the patent literature as support materials for the carbon and binder mixtures. [33b, 34, 36, 40]. These substrates continue to remain an important design option.

The practical problems in all planar cathode development programs have been in: (i) achieving high current efficiency for H_2O_2; (ii) simultaneously achieving high concentrations of H_2O_2; (iii) achieving ratios of products of general use to the paper and pulp industry (between 2.5 : 1 and 1 : 1 NaOH to H_2O_2); (iv) preventing the precipitation of sodium peroxide ($Na_2O_2 \cdot 8H_2O$) within the electrodes; and (v) demonstrating suitable electrode life at an industrially relevant current density (at least $1\,kA\,m^{-2}$). Aside from solving these problems, it is difficult to design fuel cell type electrodes for use in free electrolyte at gradients of bottom-to-top hydraulic pressure equivalent to more than about 0.2–0.3 m of electrolyte while

avoiding excessive percolation of feed gas and penetration of electrolyte to the gas plenum.

Radically different approaches have been proposed which bypass the above problems. These are primarily the particulate bed cells. However, a unique semi-horizontal cell design with wicking flow through a carbon felt cathode structure was investigated by FMC Corporation (Philadelphia, PA) [41]. Recently work has appeared on the direct generation of hydrogen peroxide at Nafion® membrane interfaces. However, the concentrations are far below the threshold of technical interest [42, 43]. Particulate electrodes in trickle-bed type electrolysers were investigated by several groups and are discussed below.

2. Trickle bed electrolysers

A successful trickle bed electrolyser was developed by Dow/H-D Tech [3, 5, 55–65]. This process for the preparation of hydrogen peroxide in caustic soda by the cathodic reduction of oxygen has been taken to small demonstration plant scale at the Fort Howard Corporation Muskogee, Oklahoma mill site [65].

The Dow/H-D Tech approach uses a particulate bed cathode of so-called 'composite chips'. The chips are granular pieces of graphite coated with a surface layer of high surface area carbon and fluorocarbon binder [57] (Fig. 1). The fluorocarbon binder is able to absorb bubbles of oxygen into its pores prior to reaction. This is particularly helpful in minimizing the need for excess oxygen. A current collector for the chips is needed, which is presumably nickel mesh
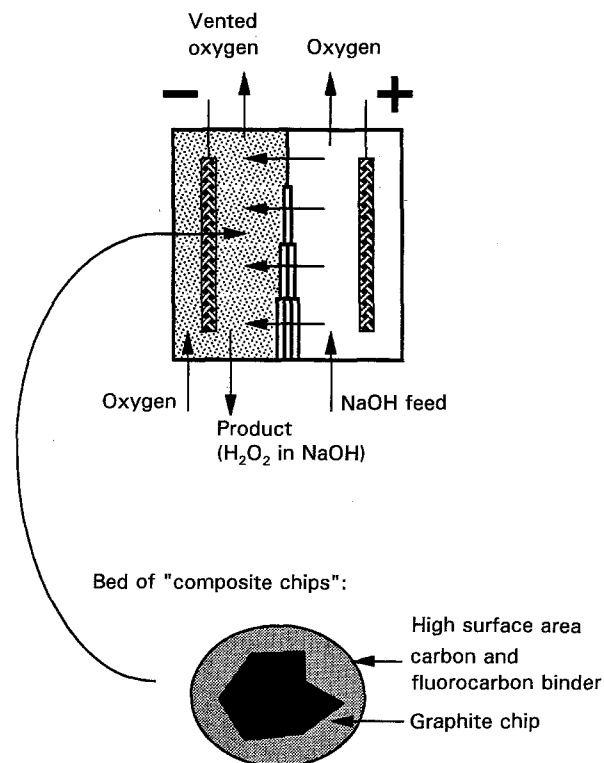

Fig. 1. Schematic of Dow/H-D Tech bipolar particulate bed diaphragm electrolyser [55–64]. Even anolyte-to-catholyte flow is achieved in tall cells by progressively increasing the number of diaphragms used.

or expanded metal. Bed thickness has been optimized considering the predominant site of reaction and electronic conductivity.

The Dow/H-D Tech process uses an inexpensive layered polypropylene microporous separator and an anolyte-to-catholyte electrolyte pressure differential to achieve a specific and uniform rate of flow between the anolyte and catholyte [59b]. The flow offsets the electromigration and diffusion of perhydroxyl ion from the catholyte to the anolyte. The process produces a by-weight ratio of approximately $1.6–1.8:1$ NaOH to H_2O_2 at concentrations of H_2O_2 of $3–4 \, w \, \%$ [64]. The current efficiency decreases as the lower ratio limit is approached. A cell voltage of $2.3 \, V$ at a current density of $0.67 \, kA \, m^{-2}$ is typical. The current efficiency declines from 95% to 80% over the six month cathode maintenance interval [64].

The $1.6–1.8:1$ ratio is limiting for direct use in many types of pulp bleaching sequences, and the concentrations would preferably be higher. In bleaching and brightening steps of mechanical pulping (generally simultaneous to, or following, caustic extraction) ratios of, on average, $0.8–1.3:1$ caustic soda to hydrogen peroxide are desired. Thus, improvements are necessary for a cathodic reduction process to broadly meet the demands of the paper and pulp industry. However, merchant hydrogen peroxide can be added to lower the ratio of electrochemically produced product.

Olomon has worked on packed bed cathodes [49, 50], and carbon felt cathodes [51, 52]. The best results are an $8000 \, h$ trial at a temperature of $60 \, ^{\circ}C$ yielding a $2 \, wt \, \%$ H_2O_2 in $6 \, wt \, \%$ NaOH product at 75% current efficiency at $1 \, kA \, m^{-2}$ with a $1.6 \, V$ cell voltage [52]. Carbon felt is said to offer less resistive loss than particulate beds. The felt is operated in a trickle bed mode, it is not used to separate catholyte from an oxygen plenum (as would be the case for a fuel cell type electrode). Olomon [49d] has patented a perforated bipole reactor geometry. This concept was operated as a stack of ten $0.4 \, m^2$ cells. The work also includes trials of coupling cathodic hydrogen peroxide synthesis to anodic chlorate synthesis [53, 54].

3. Membrane processes

Two processes by which mixtures of hydrogen peroxide and caustic soda can be made with planar cathodes in membrane-divided cells are discussed below. These involve either a caustic anolyte or an acid anolyte.

A group at Occidental Chemical (Grand Island, NY) [66–69] appear to be the first to use perfluorinated sulfonic acid membranes in hydrogen peroxide synthesis. They showed that ratios below $2:1$ can be achieved by operating an electrochemical cell with the reduction of oxygen at a fuel cell type cathode in caustic soda catholyte across a perfluorinated cation exchange membrane from an inert anode evolving oxygen in an acid anolyte.

3.1. Fuel cell-type cathodes for oxygen reduction

Fuel cell-type cathodes are continuous planar structures that have a sufficiently fine porosity coupled with sufficient hydrophobicity such that a defined catholyte compartment is isolated from a defined oxygen plenum. Ideally, there would be no catholyte seepage or oxygen bleed through. There are many ways to construct gas diffusion electrodes. Recent work on hydrogen peroxide has used materials with a carbon cloth substrate [12–15]. E-TEK adopted such a material from Prototech without change.

The Prototech cathode material used in the E-TEK studies is prepared on 'PWB-3' carbon cloth such as those from Zoltek Corporation (St. Louis, MO) or Textron Avcarb® (Lowell, MA) according to procedures given in three US Patents [71, 72]. The use of coated carbon cloth in gas diffusion electrodes is further described in a third, now expired, US patent that predates the two above [73]. PWB-3 is a densely woven 0.00040 m thick cloth that uses graphitic fibres. Typically a near 50/50 by weight dispersion of a high surface area carbon such as Cabot Corporation (Billerica, MA) Vulcan XC-72® and DuPont Teflon® 30 is prepared by ultrasonic dispersion. The resultant mixture is filtered to produce a paste. The paste is then applied to the carbon cloth via a manual coating technique wherein it is worked into both sides of the cloth as much as possible (however, still incompletely when viewed in cross section with appropriate microscopy). The loading of carbon used ranges from 45–75 g m^{-2}. Carbon/Teflon® dispersions are typically sintered at 340 °C for 20–30 min (as is commonly described in the literature [e.g., 71–75].

Carbon cloth based electrodes may have advantages over gas diffusion electrodes formed by high temperature sintering of pressure-formed carbon/fluorocarbon mixes in that the fibres of the cloth do not substantially impregnate with carbon/fluorocarbon dispersion. The resultant structure is fairly open, and wicking through fibre bundles allows enhanced diffusion of products. An analogous argument has been put forward to explain the apparent advantages of cloth based gas diffusion electrodes in fuel cells, where cathodic product water must be rapidly removed from the zone in which it is formed [76]. This may explain the apparent success of recent work [12–15] vis-à-vis extensive prior efforts, and why some previous efforts concentrated on electrodes that allowed gas percolation and electrolyte flow-through to enhance product diffusion [33c, 69].

Alternative electrode constructions were evaluated using 80 mesh nickel screen as a support and alternative high surface area carbons. The performance of the standard cloth electrode, was not equalled [13, 14].

The above cathode fabrication techniques are very different from those of the most extensively studied cathodes, where high temperature and pressure bonding and polyethylene binder materials have been used [24–32]. The polyethylene materials may allow more wetting than desirable, and pressure formation might

reduce pore size to the point that product does not diffuse out as rapidly as is required in order to avoid sodium peroxide precipitation. The same remarks apply to paraffin binders [33a]. Kastening and Faul [40] may be the first to report the advantages of fluorocarbon binders.

3.2. Caustic anolyte membrane processes

Referring to Fig. 2(a), caustic soda is fed to the anolyte which is in contact with an oxygen evolving anode. The anolyte is continuously circulated through a water cooled heat exchanger to provide cooling. A relatively high rate of flow is required due to the small permissible ΔT. Too high a ΔT may lead to the precipitation of $Na_2O_2 \cdot 8H_2O$ in the catholyte opposite the anolyte inlet. Sodium ions in the anolyte electromigrate across the membrane to the catholyte. The catholyte is fed with water after startup on dilute (1 wt %) caustic soda [13, 14]. Thereafter, enough Na^+ crosses the membrane to provide conductivity. The catholyte is in contact with the cathode which is supplied with oxygen by flow through the feed plenum. Nickel is used as a current collector for the carbon cloth cathode.

The role of the anolyte is to supply sodium ion to the catholyte. However, a sufficient resource of sodium ion is established well below the conductivity maximum. Therefore, conductivity considerations dominate, and a concentration of 20 wt % was selected [13, 14].

3.2.1. Anodes for oxygen evolution in base. Nickel 200, nickel oxide coated nickel, and Raney® nickel (a high surface area form of nickel trademarked by W.R. Grace & Co. (Baltimore, MD)) are good choices as anode material for the evolution of oxygen in base. They are inert under the desired conditions and are of low oxygen overvoltage. Nickel is noncatalytic to hydrogen peroxide decomposition. (Stainless steels are suspect due to the fact that trace amounts of iron lead to decomposition of hydrogen peroxide.) Nickel 200 expanded metal was used in the experimentation presented in Figs 3 and 5–10. It is likely that cell voltage can be reduced by 0.2–0.3 V through the use of NiO_x coated nickel or Raney nickel.

3.2.2. Membranes. Without anolyte-to-catholyte flow, perfluorinated sulfonic acid membranes must be used to isolate the catholyte from the anolyte. DuPont markets such material under the trade name Nafion®. The material is available in several different equivalent weights, thicknesses, and laminations of different equivalent weights. The most common equivalent weights are 1100 and 1500. Due to its anion rejection properties, Nafion 324 was used in most trials, as, with its reinforcing, it is strong and resists deformation. However, because these cells sandwich membranes between solid materials, unreinforced membranes are not
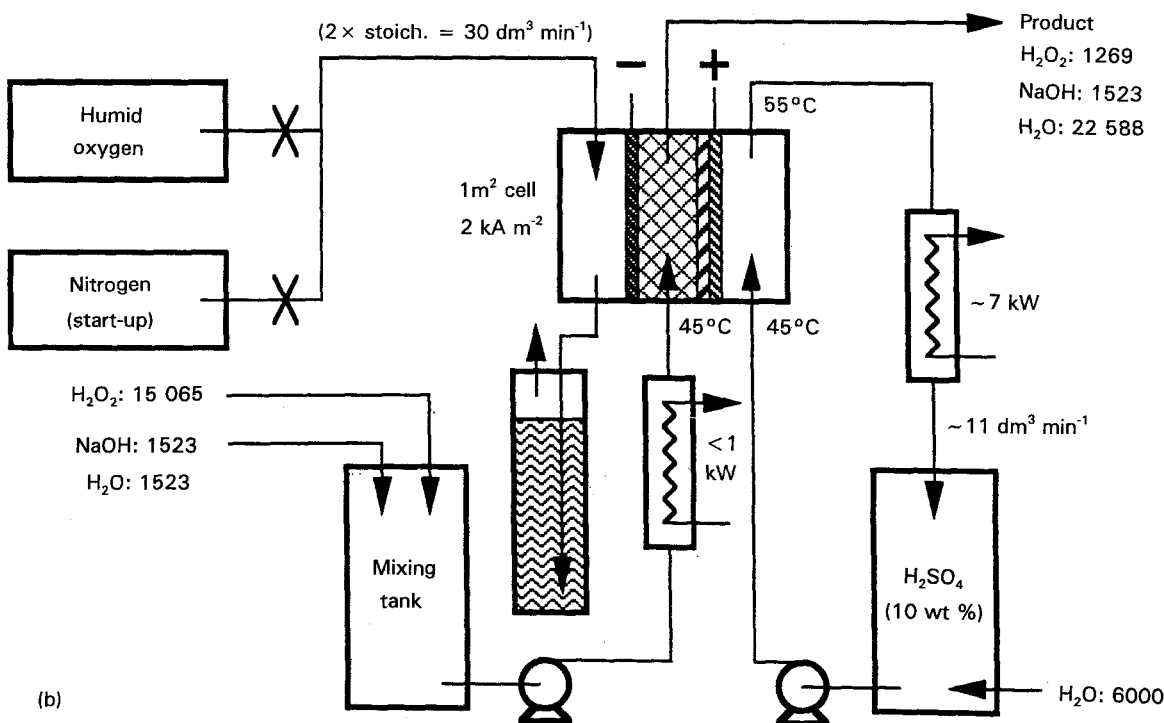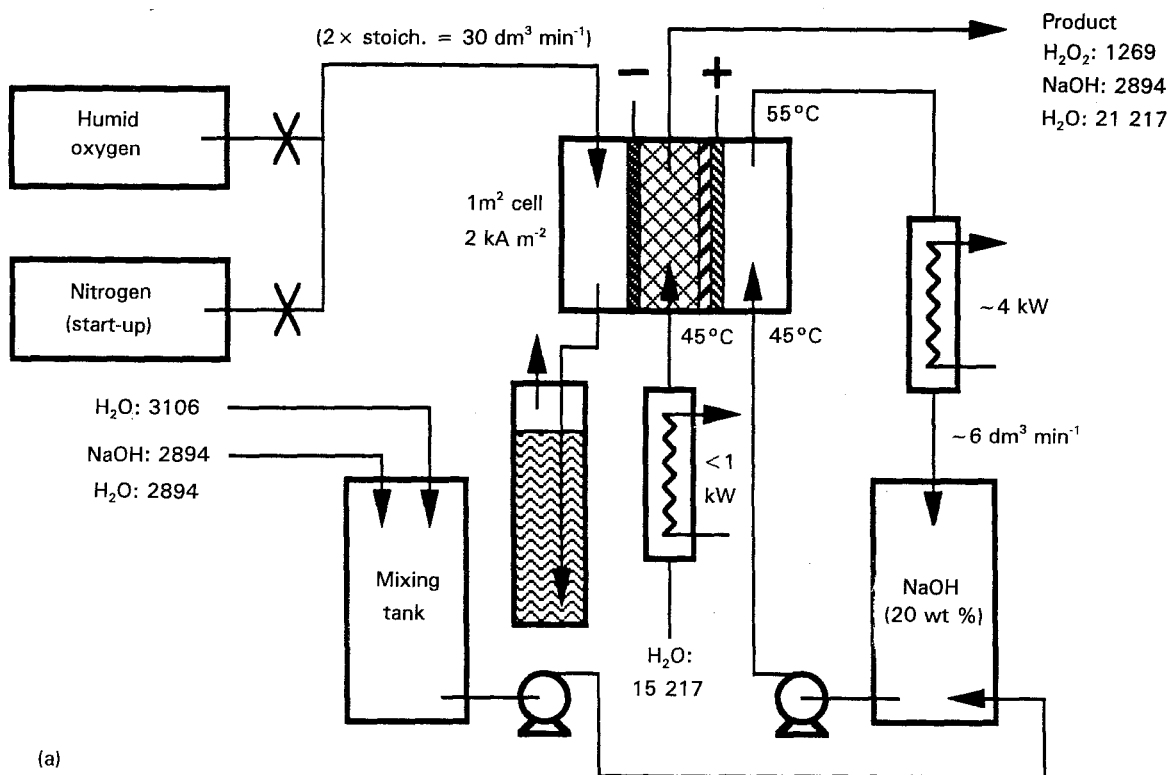
Fig. 2. Membrane cells and mass balances (a) caustic anolyte and (b) acid anolyte [12–15]. Flows are in $g\,h^{-1}$ for $1\,m^2$ cell operated at $2\,kA\,m^{-2}$ to produce $5\,wt\,\%$ H_2O_2. Basis of calculations is a theoretical 100% current efficiency.

out of the question. Grafted sulfonic acid membranes such as RAI 1010 (Pall Corporation, Haupauge, NY) are likely to be severely degraded by oxidation in less than 1000 h. Bipolar membranes are of interest, but are known not to be sufficiently oxidation resistant.

3.2.3. Operation of laboratory membrane cells. Small scale $0.010\,m^2$ test cells were constructed using acrylic endplates provided with pinfields [13, 14]. The pinfields allow for complete compression of all cell package components. The catholyte compartment was approximately 0.005 m, and was
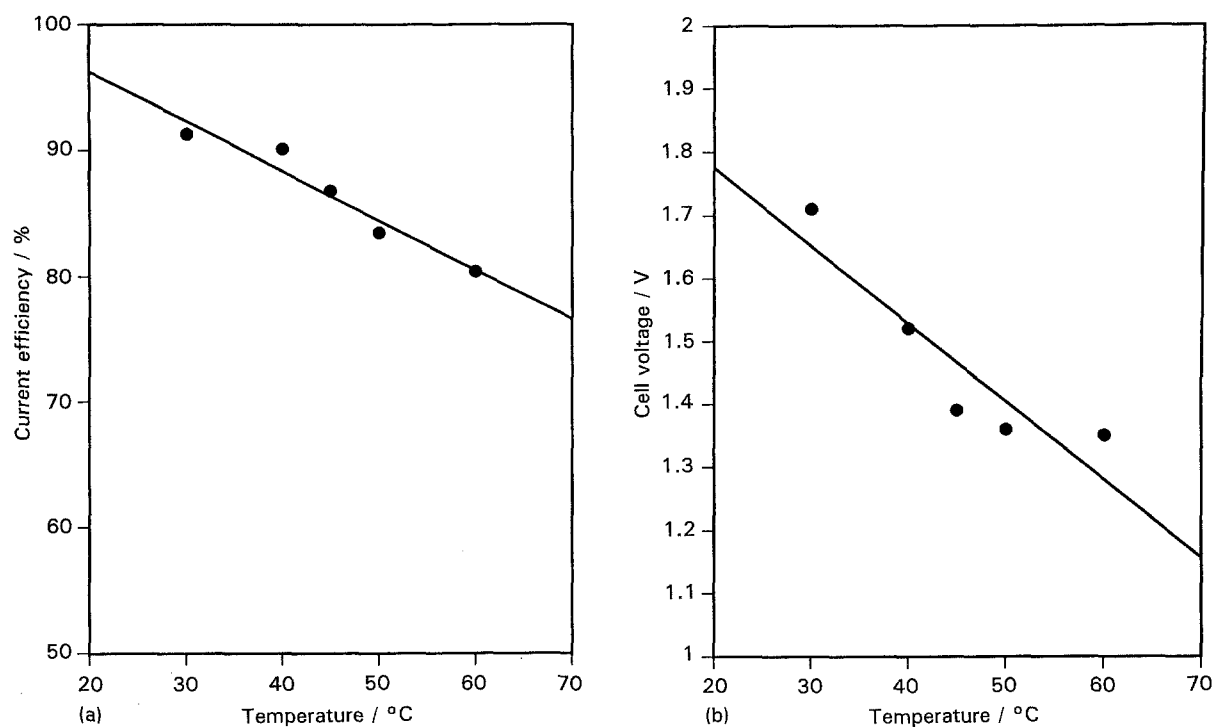
Fig. 3. Current efficiency (a) and cell voltage (b) as a function of temperature for a caustic anolyte cell operating at 1 kA m^{-2} [13–15]. Product is 2.2–2.3 : 1 NaOH to H_2O_2 at 5 wt % H_2O_2. Interelectrode gap 0.005 m.

filled with layers of expanded Teflon® sheet. The filling material provided for compression of the carbon cloth cathode against the nickel expanded metal current collector and for the uniform flow of electrolyte in the chamber. As is common procedure with gas diffusion electrodes, a coarse expanded metal and a fine mesh cathode current collector were layered together. An expanded metal anode was in contact with the membrane. The gap between anode and cathode was 0.0050 m. Though the active area dimensions were only 0.10 m × 0.10 m, three entrances and three exits were used to assure good temperature, flow and concentration distribution. These measures proved necessary for long-term operation (even at this scale) due to the volume of product.

Both anolyte and catholyte were prepared using deionized water. Both reagent grade NaOH pellets and diaphragm grade 50 wt % liquid NaOH were used [13, 14].

For 1 kA m^{-2} operation of the 0.01 m^2 experimental cells, oxygen is fed at approximately 0.20 dm^3 min^{-1}. (This is approximately twice stoichiometric. The Dow/H-D Tech process uses a 2.5 to 3 times excess, with a minimum of 1.7 [64].) Gas outlet backpressure is held at approximately 0.30 m of water by passing the effluent gas into a water column. The feed gas is humidified by passage through a gas washing bottle maintained at the temperature of the cells (45–50 °C). Temperature control and humidification appear important in controlling the precipitation of $Na_2O_2 \cdot 8H_2O$ within the cathodes. (The Dow/H-D Tech process also employs humidification [64].)

The initially hydrophobic cathodes are started by a period of hydrogen evolution into a nitrogen stream. This treatment serves to wet the macropores of the

cathodes. They are switched to oxygen as soon as a stable cell voltage is achieved. This procedure typically requires five minutes. The start-up procedure is problematic in plant practice, as nitrogen must be on-hand, and handling of evolved hydrogen must be accounted for. Once so wetted, the electrodes operate visibly wet on both sides.

A flow diagram is given in Fig. 2(a) for a 1 m^2 cell caustic anolyte cell operating at 2 kA m^{-2}. Note that the mass balance of Fig. 2(a) is constructed for 100% current efficiency. For the experimental work with cells as small as 0.010 m^2, both anolyte and catholyte must be fed using a high accuracy peristaltic pump. E-TEK used a multiple head peristaltic pump with two sizes of tubing selected to achieve the target flow rates at a common rotation rate. The incoming anolyte was heated using a Teflon® pipe wrapped with a heating tape and was maintained at 45 °C by a proportional controller. Incoming catholyte water was heated [13, 14]. A cooling heat exchanger is not necessary if the anolyte is recirculated from a volume large enough to act as a heat sink.

3.2.4. Published results.

Data published by E-TEK were developed in 0.010 m^2 electrochemical cells using Prototech cathode construction methods [13, 14, 71, 72]. These were operated on a continuous basis for 24 h per day. The cells were monitored by a data acquisition system that would automatically trip off current if the cell voltages exceeded threshold values (perhaps by hydrogen evolution) or fell beneath threshold values (perhaps by short circuits) [13, 14].

Figure 3(a) shows the effect of temperature on current efficiency. Current efficiency declines with increasing temperature. Figure 3(b) shows that cell
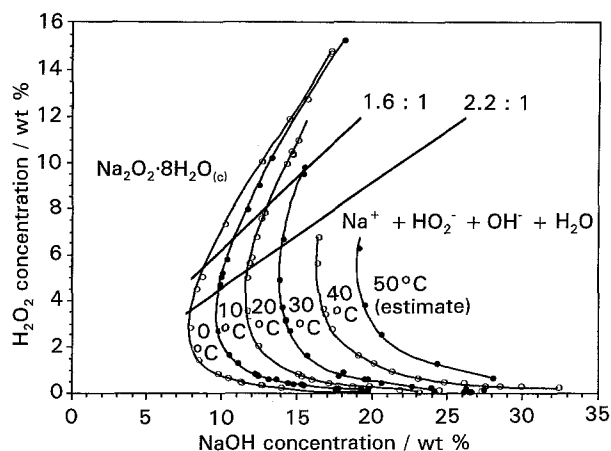
Fig. 4. Phase diagram of the system NaOH/H_2O_2/H_2O [27, 28].

voltage declines with increasing temperature. At 60 °C it is apparent that a practical limit (80% current efficiency) is reached. Thus, it is recommended that the cells be operated between 45–50 °C. Given an anolyte ΔT of 10 °C, 45–55 °C may be the best that can be managed in practice [13, 14].

Operating at a temperature above 40 °C is vital to prevent the crystallization of $Na_2O_2 \cdot 8H_2O$. Any such crystallization appears to initiate within the pores of the cathode, where under operating conditions NaOH concentrations are at their highest. Figure 4 shows the solubility of $Na_2O_2 \cdot 8H_2O$ as determined by Balej [27, 28]. Following the 2.2:1 NaOH to H_2O_2 line on the diagram, it can be seen that a temperature of at least 40 °C is required to prevent precipitation if it is assumed that the concentration internal to the electrodes is about double that of the bulk solution. Precipitation damages the cathodes by rupturing their porous structure. The damage is irreversible. Precipitation is most likely shortly after the startup of a cell, after which the danger diminishes. As apparent from Fig. 4, precipitation is only a problem with the caustic anolyte cells, in which the strength of the NaOH product is approximately 12 wt % in the case of a 5 wt % hydrogen peroxide product. The Dow/H-D Tech cells (which operate at a ratio of 1.6–1.8:1 at 3–4 wt % H_2O_2) and acid anolyte cells tuned to ratios below 1.6:1 have no such problem, as can be seen following the 1.6:1 line in Fig. 4 at 5 wt % H_2O_2.

Similar cathode damage can happen through abrasion or changing of gasketing. This is a significant problem for future cathode design.

Lohrberg and Hillrich [12], Fig. 4, shows a limitation on the hydrogen peroxide concentration of 5 wt %; this was not borne out in subsequent experimentation [13, 14].

Figure 5 illustrates E-TEKs operation of a caustic anolyte cell at 50 °C at 1 kA m^{-2} over 6000 h. The data were taken at a ratio of 2.2–2.3:1 NaOH to H_2O_2 at 5 wt % H_2O_2 concentration. The data may be used to construct a linear regression that shows that both current efficiency and cell voltage do not decay unacceptably (together within a 20% power consumption margin) over one year of 24 h per day
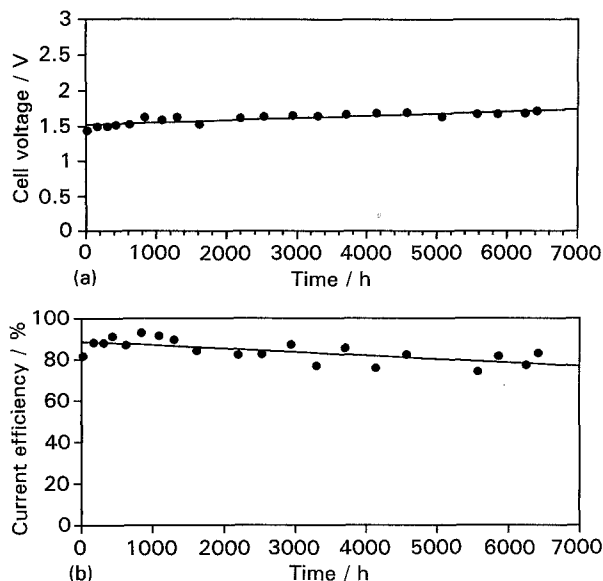

Fig. 5. Cell voltage (a) and current efficiency (b) data for the caustic anolyte cell at 1 kA m^{-2} [13–15]. Product is 2.2–2.3:1 NaOH to H_2O_2 at 5 wt % H_2O_2. Temperature 45–50 °C. Interelectrode gap 0.005 m.

unmaintained operation [13, 14]. In industrial practice it is felt 12 months of operation may be achieved with tolerable decay. (The Dow/H-D Tech brochures cite a six month cathode maintenance interval [64]). Twelve months would overlap a pulp mill's annual maintenance cycle. The hydrogen peroxide concentration selected is a key issue. If a product concentration in the 3–4 wt % range (such as produced by the Dow/H-D Tech approach) is deemed acceptable, cathode lifetime will increase. The exact cathode replacement interval is to be determined by detailed economic calculations. Figure 6 presents similar data taken at 2 kA m^{-2}. Note the higher current efficiencies (for which no satisfactory explanation is apparent). Voltage decay is more evident at this higher current density.
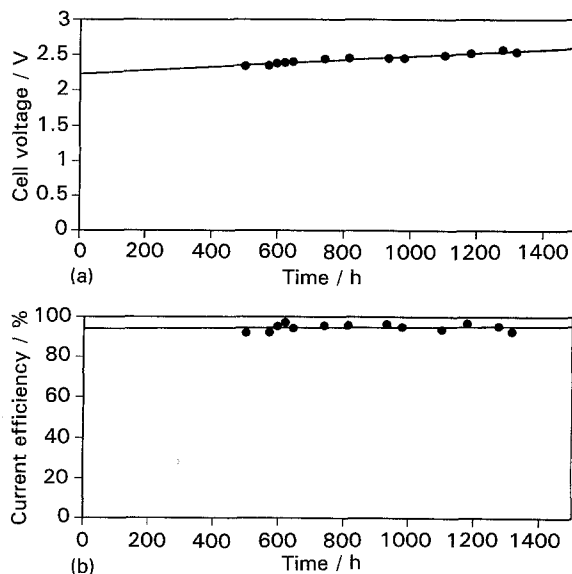

Fig. 6. Cell voltage (a) and current efficiency (b) data for the caustic anolyte cell at 2 kA m^{-2} [13–15]. Product is 2.2–2.3:1 NaOH to H_2O_2 at 5 wt % H_2O_2. Temperature 45–50 °C. Interelectrode gap 0.005 m.
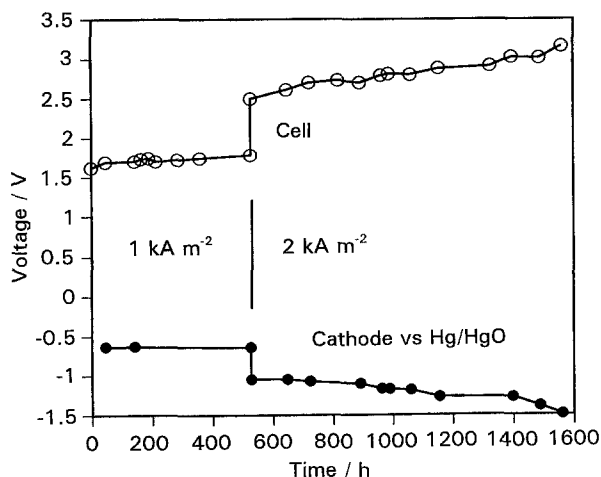
Fig. 7. Potential of the cathode against operating time at $1\,kA\,m^{-2}$ and $2\,kA\,m^{-2}$ [13]. Product is 2.2–2.3:1 NaOH to H_2O_2 at 5 wt % H_2O_2. Temperature 45–50 °C. Interelectrode gap 0.005 m.

For economic reasons it is felt that $2\,kA\,m^{-2}$, or higher, will be necessary for a viable plate-and-frame based membrane cell process. The Dow/H-D Tech approach, however, uses fairly inexpensive cell hardware at only $0.67\,kA\,m^{-2}$.

In E-TEKs experiments of Figs 5 and 6 no maintenance procedures of any kind (such as an acid treatment of the membranes to remove divalents) were performed on the cells. Thus, the cell voltage rises shown incorporate any decay of the cathodes, as well as any fouling of the membrane with divalent ions. Figure 7 shows the potential of the cathode with reference to a reference electrode as a function of operating time [13]. It is clear that the majority of the decay in cell voltage can be attributed to long-term changes taking place within the cathode. This change may be a progressive wetting of the micropore structure of the cathode caused by H_2O_2 oxidation of the high surface area carbon [13, 14]. Targeting lower H_2O_2 concentrations than 5 wt % may extend life. However, a significant distinction from the Dow/H-D Tech approach would be lost.

Cathodic decomposition of the product has not proved to be a problem. Contrary to expectations, the current efficiencies observed have been somewhat independent of cathode potential. Figure 7 confirms this.

As in the Dow/H-D Tech process, pure oxygen is preferred as feed gas because it appears to both reduce cell voltage and to extend the life of the cathodes, as is shown in the cell voltage data of Fig. 8. Oxygen is not a large component of operating cost. Operation on oxygen may extend cathode life because the zone of reaction is narrower than in the case of operation on air. If the ageing of cathodes is dependent on oxidation of the carbon of the reaction zone (which results in functionalization, and, therefore, increased wetting), then the narrow active zone may, for a longer time, be able to retreat deeper into the electrode structure, thereby finding the fresh surface necessary to maintain desirable performance characteristics.
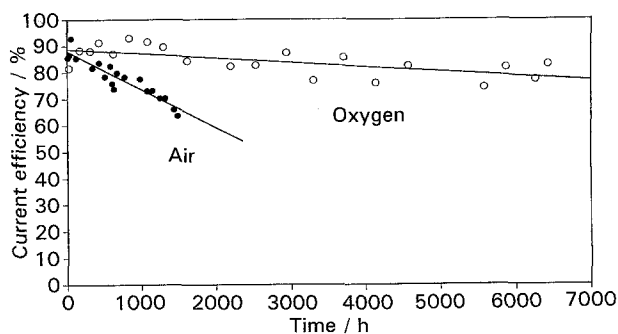

Fig. 8. Use of oxygen feed compared to the use of air feed [13, 14]. Product is 2.2–2.3:1 NaOH to H_2O_2 at 5 wt % H_2O_2. Temperature 45–50 °C.

The Prototech Company explored the effect of hydraulic head in a cell of 0.30 m height and 0.070 m width. The cell was equipped with catholyte off-takes at 0.10, 0.20 and 0.30 m [12–14]. Figure 9 shows the current efficiencies obtained by operation of the cell at the three possible electrolyte heights. At 0.30 m, current efficiency declines to about 70% despite attempts to optimize oxygen backpressure for each electrolyte height. Thus, a height limitation of perhaps 0.25 m for the original Prototech method of construction of the cathodes is apparent. This limitation may also be dependent upon the length of time the cathodes have been operated.

Even in the absence of current efficiency degradation, there would be a height limit. On the catholyte side a top-to-bottom pressure gradient is established that must be offset by oxygen pressure. A single oxygen plenum will have, comparatively, a uniform gas pressure, and thus, at some height limit, electrolyte seepage at the bottom, or oxygen percolation at the top, is inevitable.

With its packed bed particulate cathode, the Dow/H-D Tech process overcomes the height limitations of conventional planar gas diffusion electrodes. The Dow/H-D Tech process uses Celgard®, a microporous polypropylene product of Hoechst–Celanese (Somerville, NJ), as the separator material. The material is 0.0025 cm thick and is available in 38% and 45% porosity. A single layer of Celgard® does not provide sufficient restriction of cathodically formed hydrogen peroxide from the anolyte unless a pressure differential is created such that there is a
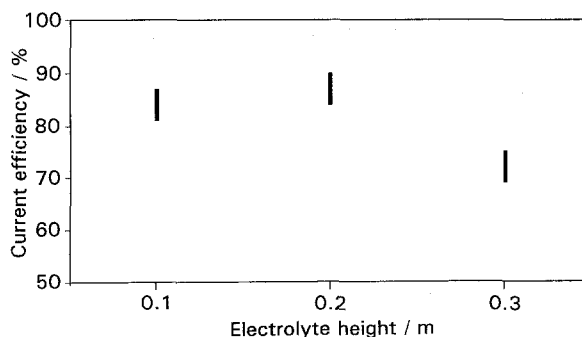

Fig. 9. Current efficiency as a function of cell height at optimized oxygen backpressure [12–14]. During operation for several tens of hours, backpressure was optimized for each depth of electrolyte within the range of 0.30 to 0.75 bar.

uniform flow of electrolyte from the anolyte to the catholyte. To build tall cells wherein the catholyte is draining to ambient pressure, Dow/H-D Tech have patented progressively laminating Celgard® such that one thickness is used at the top of the cell and up to four thicknesses are used at the bottom [59b]. This restricts what would otherwise be the tendency for greater anolyte to catholyte flow at the bottom of a tall cell.

As a comparison, using a caustic anolyte cell with a planar fuel cell type cathode and one layer of Celgard® (but without a specific flow of electrolyte from anolyte to catholyte) at $1\,kA\,m^{-2}$ and $5\,wt\,\%$ H_2O_2 less than 65% current efficiency was observed by E-TEK [13, 14].
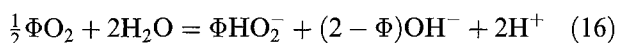
3.3. Acid anolyte membrane process

In the acid anolyte version of the process, pioneered by Occidental Chemical (Grand Island, NY) [66–69], Equations 1–4 define the cathodic process, and the anode reaction and over cell chemistry [70] are given by

Anode:

$$H_2O = \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (14)$$
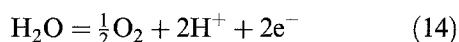
$$E/V = 1.229 - 0.0591\,pH + 0.0148\log P_{O_2} \qquad (15)$$

Net reaction:

$$\tfrac{1}{2}\Phi O_2 + 2H_2O = \Phi HO_2^- + (2 - \Phi)OH^- + 2H^+ \qquad (16)$$

Referring to Fig. 2(b), instead of water, caustic soda is fed into the catholyte compartment, where it contacts the cathode, which is provided with oxygen by flow through a feed plenum. The mass balance of Fig. 2(b) was performed for 100% current efficiency. The catholyte is isolated by the membrane from the anolyte (not now NaOH, but H_2SO_4) which is in contact with the anode which evolves oxygen and produces hydrogen ions. Hydrogen ions electromigrate across the membrane to neutralize the hydroxide ions and perhydroxyl ions formed at the cathode. Thus, the product stream is formed. All sodium ion comes from the catholyte feed stream. Perhydroxyl and hydroxyl ions are formed by the cathode in a nearly 1 : 1 molar ratio (if a 100% intrinsic cathode current efficiency). The hydrogen ion is drawn across on a 1 : 1 basis with the anions formed by the cathode. Thus, the net reaction is that only hydrogen peroxide is added to the catholyte.

The flows of the acid anolyte process are capable of being adjusted to produce product ratios as low as 0.5 : 1 NaOH to H_2O_2. The amount of NaOH in the product is set by the amount of NaOH fed to the catholyte. The net loss of sulfuric acid is less than 0.001 mol of sulfuric acid per mol of caustic soda passed through the cell, showing that Nafion® 324 forms an effective barrier to cross-membrane neutralization [13, 14]. There are limits to how low a concentration of NaOH can be fed to the catholyte. Hydrogen peroxide current efficiency does decrease

dramatically at feed concentrations much less than $5\,wt\,\%$ NaOH [13].

The cells were maintained at a desired temperature (45–50 °C) by the rapid flow of the captive anolyte through a water-cooled heat exchanger. There is less danger of precipitation (Fig. 4), and, thus, larger ΔT's are possible. Lower temperature operation may also be possible.

3.3.1. Anode materials for oxygen evolution.
The anode materials used for oxygen evolution in sulfuric acid are iridium oxide based so-called 'dimensionally stable anodes' (DSAs). These are inert metal oxide electrodes based on thermally decomposing solutions of, primarily, iridium salts with volatile anions applied to the surface of suitably-prepared oxide-free titanium. Such electrodes are expensive ($3000 for 4000 per m^2) and only forecast to have a lifetime of four years under the preferred operating conditions of $1–2\,kA\,m^{-2}$ at 45–50 °C in $10\,wt\,\%$ sulfuric acid. The lifetime of DSAs for oxygen evolution is adversely affected by current densities above $1\,kA\,m^{-2}$ and temperatures above 60 °C. These anode coatings are a major cost component of the acid anolyte process.

As in other DSA applications, new anodes appear vulnerable to leaching of iridium. This will decompose hydrogen peroxide. Therefore stabilizers must be selected for use on startup.

Anolyte concentration is not in this case selected on the basis of maximum conductivity. DSA anode life decreases with increasing acid concentration. Thus, the concentration of sulfuric acid used was $10\,wt\,\%$ [13, 14].

3.3.2. Membrane selection.
Perfluorinated membranes were again found necessary due to their oxidation resistance [13, 14]. It has been found that lower equivalent weight material is most suitable for the process. Higher equivalent weight material allows too much hydrogen peroxide loss from the catholyte to the anolyte. With 1100 EW (equivalent weight) membrane material, a fairly low equivalent weight, it becomes impossible to achieve the target ratios with hydrogen peroxide concentrations of $5\,wt\,\%$ at current densities of from $1–2\,kA\,m^{-2}$ at reasonable current efficiency. Membranes with carboxylic acid functionality to improve anion rejection in base, such as the Nafion® 900 series, cannot be used, because the carboxylic acid functionality readily protonates.

When, as in salt-splitting, it is necessary to maintain a large pH differential across a perfluorinated sulfonic acid membrane, it is important to consider the pH state of the membrane itself [77]. If the membrane is in the acidic state, HO_2^- from the catholyte will convert to H_2O_2, and, thus, without charge, the fixed charge of the membrane can no longer retard the passage of product. Unlike in salt-splitting, it is desired to pass only H^+ through the membrane (and not Na^+ in preference to H^+). Thus, the membrane has a tendency to be in the acidic state. Lower acid
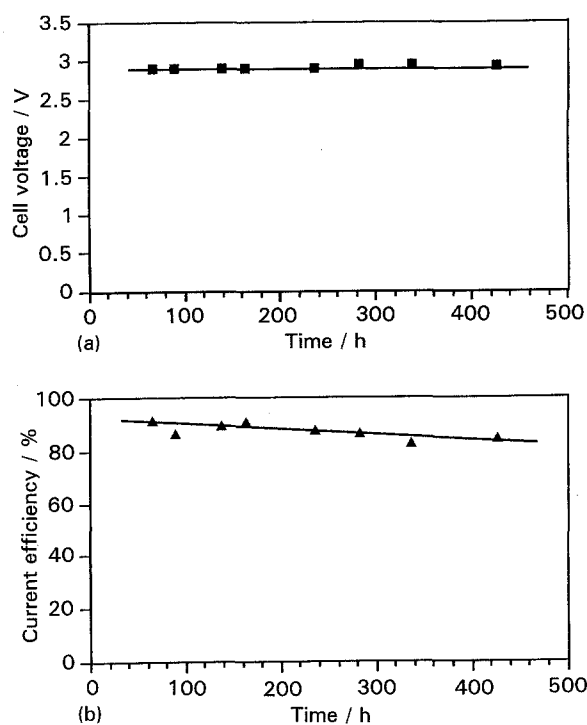
Fig. 10. Cell voltage (a) and current efficiency (b) data for the acid ano-
lyte cell at $1\,kA\,m^{-2}$ [13–15]. Product is 1.2–$1.5\!:\!1$ NaOH to H_2O_2
at 6 wt % H_2O_2. Temperature 45–50 °C. Interelectrode gap 0.005 m.

concentrations in the anolyte and lower equivalent
weight membranes may allow the membrane to
advantageously stay in the basic state, though this
has not been thoroughly investigated.

3.3.3. Published results.

Figure 10 illustrates E-TEKs
operation of an acid anolyte cell at 45–50 °C at
$1\,kA\,m^{-2}$ over 400 h of 24 h day^{-1} operation [13–15].
In this trial, the product was tuned to $1.2\!:\!1$ NaOH
to H_2O_2 at 6 wt % H_2O_2. Some rise in cell voltage
and a decline in current efficiency are noted over the
long term. The high concentration of H_2O_2
produced could have contributed to the decay
observed. As flows are adjusted to produce lower
NaOH to H_2O_2 ratios, the power consumption for
the production of hydrogen peroxide increases.

It is speculated that the decline in current efficiency
can be addressed by adjusting the porosity of the
cathode to retain an internal NaOH concentration
equivalent to that encountered in the caustic anolyte
process. Thus, the NaOH formed within the cathode
will not be able to diffuse out of the cathode as fast,
resulting in a higher internal concentration. In
practice it may be very difficult to strike a balance
between high current efficiency, resistance to precipi-
tation, and acceptable hydraulic characteristics at
0.20–0.25 m cell height.

3.4. Product ratio variation

Using the caustic anolyte membrane process the ratio
of products lies in the narrow range of 2.2–$2.3\!:\!1$
NaOH to H_2O_2. This product ratio is too high to
satisfy many paper and pulp bleaching sequence
requirements, however, it is apparently of some use

in Kraft hydrogen peroxide enforced alkali extrac-
tion, in deinking of recycled paper, and in the
bleaching of textiles.

Thus, it is of interest to consider ways of combining
add-on processing to examine whether it is feasible to
have the flexibility to lower product ratios (for exam-
ple to $1.2 \pm 0.3\!:\!1$). A key question is whether such
lower ratios can be produced less expensively than
via use of the acid anolyte process. Combinations
with the caustic anolyte based processes were thus
considered [13, 14], and it was suggested that coup-
ling diaphragm or membrane caustic anolyte pro-
cesses with the acid anolyte membrane process may
be of interest.

The caustic anolyte cells are of lower capital cost
than those of the acid anolyte process because the
nickel anode material is far less expensive than iridium
oxide DSAs. The materials of construction need only
be resistant to caustic soda rather than sulfuric acid,
which allows the use of less expensive materials.

Caustic anolyte cells are also of lower operating
cost due to lower cell voltages. There are no large
concentration polarization losses caused by the
approximately 14 pH unit change across the mem-
brane in an acid anolyte cell. (Thermodynamically
this gradient alone contributes approximately 0.8 V
to the cell voltage.) The caustic anolyte type cells
have a catholyte concentration of 11–13 wt %
NaOH at a product concentration of 5 wt %. The 11
to 13% concentrations are dramatically more conduc-
tive than the approximately 6 wt % NaOH catholyte
concentrations that acid anolyte cells typically must
use in order to achieve lower product ratios of, for
instance, $1.2\!:\!1$ at H_2O_2 concentrations of 5 wt %.

There are two distinct ways by which to couple acid
anolyte cells and basic anolyte cells to reduce capital
and operating costs. The output streams of the two
types of cells can be merely mixed. Or, more advanta-
geously, the catholyte output of the caustic anolyte
cells can be fed as the catholyte input of the acid
anolyte cells to develop an increased hydrogen per-
oxide concentration without the addition of sodium
ion [13, 14].

The above method is preferred over simply mixing
the products of the two types of cells because it has
been found that the power consumption of the acid
anolyte process increases as the flows are tuned to
achieve lower product ratios. Thus, it is undesirable
to produce a very low ratio product (e.g., $0.5\!:\!1$
NaOH to H_2O_2) in order to mix it with a high ratio
product (e.g., $2.25\!:\!1$ NaOH to H_2O_2) in order to
produce an intermediate ratio product (e.g., $1.2\!:\!1$
NaOH to H_2O_2).

To produce a $1.2\!:\!1$ by-weight ratio of caustic soda
to hydrogen peroxide at 2.02 M (7.5 wt %) NaOH and
1.85 M (6.25 wt %) H_2O_2, a caustic anolyte product of
2.82 M (10.1 wt %) NaOH and 1.41 M (4.75 wt %)
H_2O_2 may be enriched with 0.83 M H_2O_2 through
the operation of the acid anolyte cell. Thus, 45% of
the total hydrogen peroxide requirement comes
from the acid anolyte cell and 55% of the hydrogen

peroxide requirement can be generated from the less expensive caustic anolyte process.

Both PAPRICAN (the Pulp and Paper Research Institute of Canada, Pte. Claire, Québec) [78] and Dow/H-D Tech [79] hold patents in the area of extracting NaOH from product. The PAPRICAN approach uses bipolar membrane technology. However, the oxidation resistance of current bipolar membranes is likely to prove insufficient. Both processes consume power without producing more hydrogen peroxide, as in the alternative strategy discussed above.

3.5. Product stability

The half-life of the 2.2–2.3 : 1 product under ideal (rather than realistic) conditions, wherein it is stored in a new brown polyethylene bottle isolated from light, heat, and mechanical agitation, is of the order of 30 days [13]. This sort of stability is much better than expected in a real environment. It does, however, show that the hydrogen peroxide generation process itself poses no limitations on stability of practical importance. The stability of hydrogen peroxide generated in the catholyte of either an acid anolyte or a caustic anolyte cell is stable enough to allow passage through a second electrolytic cell.

The catholyte flows through the catholyte compartments on a single pass basis in order to avoid decomposition of the hydrogen peroxide caused by mechanical agitation. Stabilizers may be added. EDTA (0.002 wt %) is added to the caustic fed to the Dow/H-D Tech process [64]. Iron is one of the principle contaminants that must be isolated through the use of additives. The use of silicate additives to stabilize hydrogen peroxide is thoroughly treated in an ACS Monograph [80]; however, little information is available on highly alkaline conditions. A Canadian patent has recently issued on the use of stabilizers for alkaline conditions [81]. Magnesium has also been suggested in the literature [82], and features in Dow/H-D Tech literature as an additive to the product liquor [64].

4. Approaches of scale-up membrane processes

In accordance with Prototech results, Lurgi AG (Frankfurt) has taken the approach of adapting their tall chlor-alkali cell by subdividing it into several tiers [12]. The oxygen feed plenum is unsegmented although the catholyte plenum is subdivided to stay within electrolyte height guidelines. The approach is well-known, as Eltech Research Company (Fairport Harbor, OH) used a similar design in their early 1980s chlor-alkali pilot plant which incorporated air cathodes [84]. Internal sealing difficulties and control complexity are inherent in such a design.

The authors have performed a design study using the ICI Chemicals and Polymers Ltd FM21-SP monopolar chlor-alkali electrolyser as a candidate for retrofit to the production of on-site hydrogen

peroxide in caustic soda [16] (Fig. 11 [83]). The FM21-SP cell has an active area height of 0.25 m and an active length of 1.0 m. The cell height was judged the best of commercially available hardware for the operation of gas diffusion electrode processes not using membrane/electrode laminations.

The FM21-SP features top and bottom current feeder busses and six internally manifolded ports capable of handling three flows. One of the port combinations was intended to serve as balance headers in chlor-alkali use. These can be conveniently used for oxygen flow. The balance ports cannot, as designed, provide for top-to-bottom or bottom-to-top flow. Internal dip tubes may, however, be used for exiting oxygen.

The hydrogen peroxide process requires anolyte, catholyte, and oxygen flow. Oxygen flow can be side-to-bottom through the centre of a lantern blade, anolyte flow can be bottom-to-top, and catholyte flow can be bottom-to-top, bypassing the use of the balance header ports (an external manifolding system was used). These arrangements require a retrofit of the FM21-SP involving the custom moulding of its gasket seals.

For the production of hydrogen peroxide, the FM21 must be retrofitted with a catholyte compartment. For experimental purposes, the compartment can be initially built with top and bottom flow distribution manifolds. The catholyte compartment can be filled with Teflon®, PVDF, or PVC three dimensional mesh (demister-type) material in order to compress the carbon cloth cathode to a nickel lantern blade current collector. Woven nickel may also be used. Oxygen flow was provided to the interior of this lantern blade. Figure 11 shows cross-sections of the FM21-SP as modified for initial trials of the hydrogen peroxide process.

It was found that the standard cathodes allowed for some percolation of oxygen from the gas plenum into the catholyte compartment [14, 15]. This may be reduced through cathode redesign, and then the thickness of the catholyte compartment can be substantially reduced if there is a reduced need for gas removal. For cell voltage data to reproduce the performance of the 0.010 m² laboratory cells, the 0.015 m forecast to be now needed for catholyte compartment gap needs to be reduced to 0.003 m [15].

A single cell of the FM21-SP is regarded as a useful tool for evaluating the ·hydraulics of full-scale cathodes, sealing techniques, and means of current distribution to the cathodes.

5. Process economics

The economics of the Dow/H-D Tech particulate bed process have been reported upon by SRI International (Menlo Park, CA) [3] and CPI Consulting (White Plains, NY) [5] in detail far beyond the scope of this review. Dow also supplies an economic analysis [64]. The analysis given by SRI International shows that
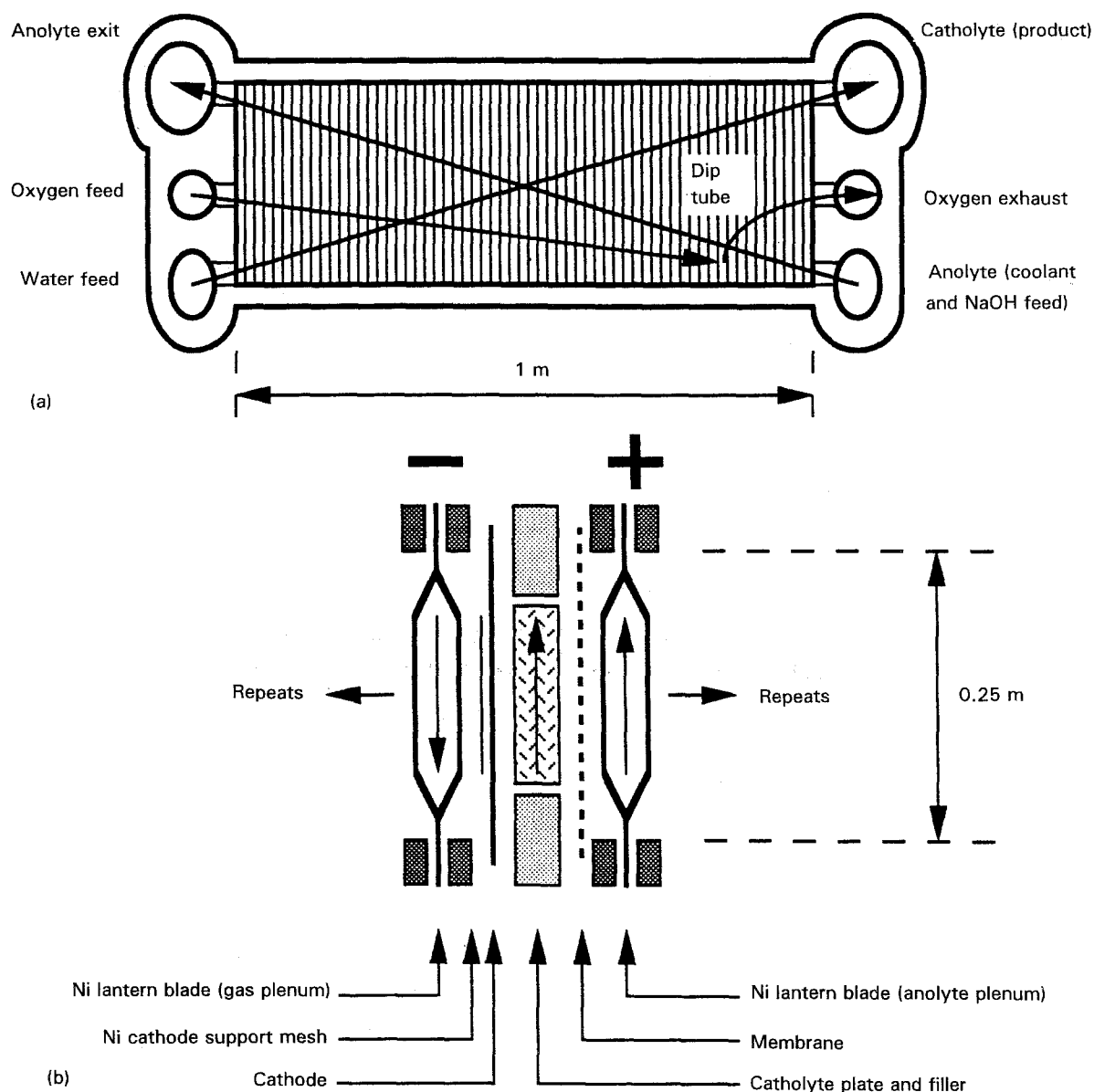
Fig. 11. Modified Imperial Chemical Industries FM21-SP Chlor-Alkali Electrolyser [16]. Adapted from [83]. (a) 'Lantern blade' and flows; (b) cross-section of assembly.

there is a cost to mixing of reagents; thus, one should not compare to merchant chemical pricing alone.

Table 1 lists the assumptions used for process characteristics in the comparisons to follow.

All costing is based on either a production rate of 5 or $10 \, \text{mT yr}^{-1}$ of 100% hydrogen peroxide (assuming 350 day operation). Interest charges of 7.5% are included, and capital charges are based on straight-line depreciation over ten years with no salvage value.

Costs for caustic soda are not included as this would be common to either utilizing these processes or purchasing hydrogen peroxide from a merchant facility.

Power consumption for all cases is based on an estimated average performance based on an assumed one year cathode life. The model assumes $0.03 \, \$(\text{kWh})^{-1}$ power. In certain areas, such as the US Pacific Northwest, Canada and the US South, power is available under long-term contracts at such levels.

Table 1. Assumptions used in economic comparisons

Performance assumptions	Dow/H-D Tech (Diaphragm)	Alkaline anolyte (Membrane)	Acid anolyte (Membrane)
Current density (kA m^{-2})	0.67	2	2
Voltage (V)	2.4 (lifetime)	2.2–2.3 (lifetime)	3.5–4 (projected)
Current efficiency (%)	85 (lifetime)	85 (lifetime)	70 (projected)
Concentration (wt %)	3–4	5, less is better	5, less is better
Cooling	water to hold 20 °C	water to hold 45–50 °C	water to hold 45–50 °C
Cathode* life (years)	0.5	1	1

* Assumed from maintenance interval given in [64].

Table 2. Estimated process economics for base and acid anolyte membrane cell processes

Capacity	Unit costs (Notes)	Base anolyte (Product ratio = 2.25 : 1)		Acid anolyte (Product ratio = 1.2 : 1)	
Variable operating cost		$5\,mT\,day^{-1}$	$10\,mT\,day^{-1}$	$5\,mT\,day^{-1}$	$10\,mT\,day^{-1}$
Oxygen	$0.11 kg^{-1}	100 500	201 000	100 500	201 000
Electricity	$0.03 kWh^{-1}	230 500	461 000	467 250	934 500
Process water	$0.0001 kg^{-1}	5000	10 000	5000	10 000
Cooling water	$0.00001 kg^{-1}	10 000	20 000	10 000	20 000
Total (no NaOH charges)	$ yr^{-1} (350 days)	346 000	692 000	583 000	1 166 000
Fixed operating cost		$5\,mT\,day^{-1}$	$10\,mT\,day^{-1}$	$5\,mT\,day^{-1}$	$10\,mT\,day^{-1}$
Manpower:					
Operation	man-years	1	1	1	1
Maintenance	man-years	1	2	1	2
Labour	$ yr^{-1}	80 000	120 000	80 000	120 000
Area of cells	m^2	193	386.5	235	470
Cathodes + (acid) anode coating + membrane	$350 m^{-2} + 1/4 ($2500 m^{-2}) +1/3 ($750 m^{-2})	116 000	231 500	288 000	576 000
Insurance, Taxes, misc.	2.0% of capital	74 000	106 000	78 000	116 000
Other maintenance	1.5% of capital	55 500	79 500	58 500	87 000
Total	$ yr^{-1}	245 500	417 000	424 500	779 000
Capital cost		$5\,mT\,day^{-1}$	$10\,mT\,day^{-1}$	$5\,mT\,day^{-1}$	$10\,mT\,day^{-1}$
Cells*	at $6000 m^{-2}	1.2 million	2.3 million	1.4 million	2.8 million
Ancillaries & Engineering	$	2.5 million	3.0 million	2.5 million	3.0 million
Subtotal	$	3.7 million	5.3 million	3.9 million	5.8 million
7.5%, 10 Year amortization	$ yr^{-1}	527 000	755 000	556 000	826 000
Total cost	*$ yr^{-1}* *$ kg^{-1}*	*1 118 000* **0.64**	*1 864 000* **0.53**	*1 563 000* **0.89**	*2 771 000* **0.79**

* Calculated from Dow brochure [64].

Table 2 shows estimated economics for the caustic anolyte and acid anolyte processes at 5 and $10\,mT\,day^{-1}$ [16].

If inexpensive ($6000\,m^{-2}$) cell hardware is possible, the planar cathode caustic anolyte membrane cell process has scope to compare favourably with the Dow/H-D Tech economics [64]. If such a cell is not possible, the economics shift substantially in favour of Dow/H-D Tech.

Table 3 shows the general conclusions of the economic analysis and how the membrane processes compare to the Dow/H-D Tech process [16].

The foregoing calculations are presented as an analytical tool only, and contain many assumptions, some of which may not hold over the course of further development. Custom designed cells may be necessary

to meet the $6000\,m^{-2}$ level. These will probably have to be bipolar. Current densities of at least $2\,kA\,m^{-2}$ are required. The acid anolyte membrane cell process may only be of interest in remote sites, or in use in combination with other technologies as a means of lowering product ratio, as is discussed below.

Low ratios NaOH to H_2O_2 may be produced by the cascaded coupling of either diaphragm or membrane caustic anolyte cells and acid anolyte cells. Rough costs for various product ratios may be interpolated from the economics in Table 3.

6. Future work

If justified by an up-turn in hydrogen peroxide pricing, the continued absence of small-scale anthroquinone

Table 3. Comparison of Dow and membrane cell processes

General conclusions	Dow/H-D Tech (Diaphragm)	Alkaline anolyte (Membrane)	Acid anolyte (Membrane)
Power consumption (AC $kWh\,kg^{-1}$ H_2O_2)	4.4	4.4	8.9
Concentration (wt %)	3–4	5, less is better for electrode life	5, less is better for electrode life
Ratio range (NaOH to H_2O_2)	1.6–1.8 : 1, variable	2.2–2.3 : 1, fixed	1.0–1.2 : 1, variable
Net operating cost, ($ kg^{-1})	0.62 ($10\,mT\,day^{-1}$)	0.53 ($10\,mT\,day^{-1}$)	0.79 ($10\,mT\,day^{-1}$)
(100% basis)	0.75 ($5\,mT\,day^{-1}$)*	0.64 ($5\,mT\,day^{-1}$)	0.89 ($5\,mT\,day^{-1}$)

* Calculated from Dow brochure [64].

plants in the marketplace, and a clear niche in view of the success of the Dow/H-D Tech process, commercial hardware may be either developed or retrofitted for planar gas diffusion electrode membrane cell processes. The key issues in a full-scale membrane cell testing program are the following: (i) current collection via pressure contacting and the resultant current distribution; (ii) uniformity of flows and concentration distribution; (iii) optimization of gas percolation to the catholyte and electrolyte seepage to the gas plenum; and (iv) uniformity of catholyte temperature due to sensitivity to sodium peroxide precipitation.

Improvements are needed in the adherence of carbon/fluorocarbon filler to substrate materials and the gas/electrolyte pressure differential tolerance of cathode materials. Lifetime improvement can probably be addressed by variations of the carbon type used in the reaction layer of the cathodes, and possibly by increasing electrode thickness (thus, providing additional reaction layer). Thickness may be best added by starting with thicker substrate materials such as nickel gauze, though valuable wicking properties may be lost. Added thickness may, however, aggravate precipitation problems and dictate operation at lower concentrations. Whatever strategy is chosen, further electrode development can only be meaningfully carried out in full-height cell segments.

The use of more sophisticated anode coatings and alternative membranes should also be explored. Dow Chemical (Midland, MI), Tokoyama Soda (Japan), Asahi Glass (Japan), Asahi Chemical Industry (Japan), and Chlorine Engineers (Japan) have developed analogs to DuPont's Nafion®. Some of these are available with properties outside of the normal range of commercial Nafion®.

A further reference to the Dow/H–D Tech process has appeared whilst this manuscript was in proof [85]. This gives certain performance parameters for the Dow process which must be compared very carefully to the economic analyses distributed by Dow; among these is a 1.5 year cathode life.

7. Conclusions

Planar fuel cell type electrodes may be suitable for the cathodic reduction of oxygen to hydrogen peroxide and can be used to synthesize ratios of caustic soda to hydrogen peroxide of interest to the paper and pulp industry. The problems of $Na_2O_2 \cdot 8H_2O$ precipitation and achieving acceptable product concentrations and ratios have, in principle, been overcome. It now remains to install such electrodes in full-scale cells of dimensions similar to the FM21-SP and to tailor electrode composition and hydraulic balances so that an acceptable gas percolation/electrolyte penetration balance is achieved. It may be found that a different electrode design will be required for realistic height cells and that this may negate all small-scale testing to date performed by Prototech and E-TEK. In the case of acid anolyte cells, more

experimental work focusing on membrane trials is necessary to improve current efficiency. At least in the case of the Dow/H-D Tech particulate bed cathode processes, with higher hydrogen peroxide pricing, and means of addressing product ratio limitations, a new and environmentally important electrochemical process may become commercially successful.

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