SCALE-UP OF THE PERFORATED BIPOLE TRICKLE BED ELECTROCHEMICAL
REACTOR FOR THE GENERATION OF ALKALINE PEROXIDE

by

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Abstract

Conventional electrochemical reactors generating alkaline hydrogen peroxide by electro-reduction of oxygen use three-dimensional electrodes in mono-polar cell stacks that operate near atmospheric pressure. The available commercial electrochemical process (eg. the Dow-Huron trickle-bed cathode) is limited to a current density of about 1 kA m^{-2} , while other systems under development (eg. the Kvaerner-Chemetics gas diffusion cathode) run at current density up to about 2 kA m^{-2} . This relatively low current density results in a high capital cost that limits the use of the electrochemical process as an alternative to the commercial thermochemical process that obtains hydrogen peroxide by the auto-oxidation of anthraquinols.

The limitations to the current density in the electrochemical processes operating near atmospheric pressure are largely due to oxygen mass transfer constraints. To increase the oxygen mass transfer rate work has been done at UBC with a bipolar electrochemical reactor that runs at 800-1200 kPa. As opposed to other systems the UBC process uses a relatively simple cell configuration in which a single electrolyte flows with oxygen gas in a graphite felt cathode, sandwiched between a microporous diaphragm and a bipolar electrode plate. To compete with the commercial thermochemical process such an electrochemical reactor should operate with good current efficiency and low voltage (e.g. $> 80 \%$, $< 3 \text{ Volt}$) at current densities above 3 kA m^{-2} .

The anodic generation of oxygen in the UBC system at current density above ca. 2 kA m^{-2} is a problem as it inhibits the passage of current and compromises the performance of the reactor. To circumvent this problem of anode resistance experimental work was done on a perforated bipole electrochemical reactor that allows oxygen disengagement on the anodes through the perforations into the adjacent cathode bed. These perforations also allow current by-pass that translates in to a loss in current efficiency. As a guide to the development and scale-up of this system a two-cell bipolar electrochemical reactor was modelled with trickle-bed cathodes and the current by-pass through the perforated bipole accounted for. The predictions of this model were

compared to the performance of a bench scale reactor operating at current density up to 5 kA m^{-2} and used to optimize the bipole configuration.

The reactor was eventually scaled-up from small scale (120 mm length by 25mm width and superficial electrode area $30\text{e-}4 \text{ m}^2$) to medium scale (630 mm length by 40 mm width and superficial electrode area $200\text{e-}4 \text{ m}^2$) for two cells. The current efficiency for peroxide generation on the two-cell medium scale reactor was very encouraging ($\sim 80\%$ at 5 kA m^{-2}) and the voltages obtained were also in the desired range ($\sim 3.2 \text{ V}$ per cell at 5 kA m^{-2}).

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CHAPTER 1

Introduction

1.1 The importance of hydrogen peroxide in the pulp and paper industry

The production of pulp and paper is a major commercial enterprise with worldwide economic and environmental consequences. According to 1994 statistics there were some 4500 pulp and paper plants around the world producing ca 300 million tonnes per year of products. The total worth of these products was estimated to be ca US \$250 billion per year. The cost of chemicals used in the industry amounted to ca US \$10 billion per year [Oloman, 1996]. Therefore the impact of reducing the cost of chemicals used in the industry can be substantial.

Pulp bleaching is one of the cost intensive areas of pulp and paper processing and a reduction in cost of chemicals used in bleaching would impact the entire industry. The growing need for a cleaner environment and the stringent regulations being imposed by the EPA to dispense with chlorine based chemicals, demands an alternative. In this scenario H_2O_2 with its benign nature, is a good candidate.

There is a worldwide trend towards phasing out chlorine based chemicals from the chemical industry as these chemicals have been declared global pollutants. Finland, for instance, has already adopted a policy of dispensing with both elemental chlorine as a bleaching agent (ECF- Elemental chlorine free) and also chlorine based chemicals (TCF- Total chlorine free). North America has also abandoned the use of Cl_2 as a pulp bleaching agent. The chemicals that have benefited most from this shift away from Cl_2 are sodium chlorate and hydrogen peroxide. Sodium chlorate ($NaClO_3$) is used to generate on-site chlorine dioxide (ClO_2) which is used alone and in conjunction with hydrogen peroxide for a variety of pulp bleaching applications.

The importance of hydrogen peroxide may be understood from the variety of its applications in the pulp and paper industry.

1.2 Hydrogen peroxide as a bleaching agent

Hydrogen peroxide is widely used in the pulp and paper industry as a bleaching and brightening agent. Peroxide was first used for the brightening of mechanical pulps (high yield pulps); then for the delignification and the bleaching of the chemical pulps (pulps resulting from kraft or sulfite processes) then finally for the brightening of reclaimed fibres from the recycling of papers.

Today, hydrogen peroxide is the only bleaching/brightening agent used in all processes and in the production of both mechanical and chemical pulps from hardwoods and softwoods as well as annual plants such corn and rice straws.

1.2.1 Mechanical pulp brightening

In the manufacturing process of mechanical pulps, i.e., SWG pulp (Stone Wood Ground), TMP pulp (Thermo Mechanical Pulp), CTMP pulp (Chemi Thermo Mechanical Pulp) and APMP pulp (Alkaline Peroxide Mechanical Pulp), peroxide plays a key role in developing the right optical characteristics and in safeguarding these pulps mechanical characteristics.

For more than ten years, considerable efforts have been made by the industry to reduce the energy consumption in processes used for the production of mechanical pulps. By pre-treating the chips with hydrogen peroxide before refining or by direct introduction of hydrogen peroxide in the refiners, a decrease in specific refining energy consumption and the development of better physical properties of the pulp were observed.

Hydrogen peroxide remains the principal brightening agent for mechanical pulps. Applied alone or in combination with other bleaching agents, peroxide allows the

production of pulps of very high levels of brightness. Conventional peroxide brightening is done at 10 to 20%_w pulp consistency, using a charge of 1 to 3%_w H₂O₂ at 40-60 °C for 1 to 3 hours [Oloman, 1996].

1.2.2 Chemical pulp bleaching

Chemical pulps are mainly obtained starting from the Kraft manufacturing process. The pulps resulting from cooking are thereafter delignified and bleached according to two processes called the "Elemental Chlorine Free" (ECF) and "Total Chlorine Free" (TCF) processes. Hydrogen peroxide is the principal bleaching agent in TCF sequences where it can be associated with oxygen, ozone or peracids for the manufacture of chemical pulps of very high degree of brightness having good physical properties. In ECF bleaching, considered as a Best Available Technology (BAT) in the U.S.A., hydrogen peroxide is used in the alkaline extraction stages to increase the effectiveness of delignification [Taylor, 1998].

Hydrogen peroxide is also used for the manufacture of peracids, such as peracetic acid, that are used for delignification and bleaching of the chemical pulps. The peracids, whose chemistry of bleaching is similar to hydrogen peroxide, have a higher oxidizing potential towards wood components.

Hydrogen peroxide can also be used as an reducing agent in acid medium for the generation of chlorine dioxide (ClO₂) starting from sodium chlorate. Hydrogen peroxide is a substitute for the usual reducing agents such as sulphur dioxide (SO₂).

Hydrogen peroxide can be used in the processing of odours, in particular for processing the condensates that contain many sulphur derivatives such as mercaptans, sulphides or disulfides. The oxidizing power of peroxide is particularly well adapted to deal with problems of air pollution.

Lastly, hydrogen peroxide can be used as an antichlor agent for the liquid waste generated from chlorine or chlorine dioxide bleaching processes.

1.2.3 Recycled pulp bleaching

Hydrogen peroxide is used in bleaching pulps resulting from the recycling of old paper. Hydrogen peroxide is introduced during the stages of slow or rapid dispersion of inks where peroxide allows a better elimination of residual inks. The effect of hydrogen peroxide bleaching is advantageous after post-flotation. Lastly, used as a bleaching agent, alone or in combination with other oxidizing or reducing agents, hydrogen peroxide produces recycled fibres with very high levels of brightness.

Considering the importance of peroxide in all the aforementioned processes, its manufacture is critical to the economics of the pulp and paper industry.

1.3 Manufacture of hydrogen peroxide

1.3.1 Thermochemical synthesis

Traditionally, over 90% of H_2O_2 is manufactured using a thermochemical process that generates peroxide by the autooxidation of anthra-quinols. The autooxidation process was developed in the 1940's in Germany. This is a cyclic process wherein a working solution containing an alkyl anthraquinone is sequentially hydrogenated, oxidized, subjected to an extraction process, and recycled back to the hydrogenation step.

In the hydrogenator, alkyl anthraquinone undergoes hydrogenation in the presence of Raney Ni or Pd based catalysts. The resulting solution containing hydrogenated alkyl anthraquinone is filtered to remove the catalyst and is fed to the oxidizer as shown in Figure 1.1. The alkyl anthraquinone reacts with air or oxygen to form hydrogen peroxide and regenerate the alkyl anthraquinone. In the extraction step, demineralized water is added to extract crude aqueous hydrogen peroxide of ca 20%_w concentration, leaving the

alkyl anthraquinone working solution for recycle to the hydrogenator. The crude peroxide is purified, concentrated and stabilized to produce the 35-70%_w merchant H₂O₂ [Dence & Reeve, 1996].

Fig. 1.1 Flow sheet for anthraquinone-based hydrogen peroxide production [Dence and Reeve, 1996]

A common technical challenge for the catalytic anthraquinone process is the possibility of excessive hydrogenation of the aromatic ring, leading to low selectivity for anthraquinol and the associated contamination of the working solution by undesired byproducts of hydrogenation.

The autooxidation process involving catalytic anthraquinone is a multi-step, capital intensive process. As most of the pulp mills are scattered across North America

and the world, an onsite process for hydrogen peroxide generation would provide the industry with more flexibility in operation as well as eliminating the need for hydrogen peroxide storage and transportation. This sort of flexible, low capital cost process may be possible using an electrochemical synthesis method.

1.3.2 Electrochemical synthesis

For most applications, the pulp and paper industry needs alkaline peroxide in dilute concentrations (ca 3%_w H₂O₂, see section 1.2.1) for bleaching and brightening applications. Such concentrations are possible by generating hydrogen peroxide using an electrochemical route. The electrochemical route is likely to be competitive only at low peroxide capacity (< 10 tonnes/day) and in plants located in remote locations where the cost of transportation is high.

The electrochemical processes for peroxide in general involve O₂ electroreduction to H₂O₂ on carbon based porous cathodes, in various flow arrangements such as the trickle flow mode or gas diffusion mode, usually in alkaline solutions.

One such route is the Dow-Huron process. This is so far the only commercial electrochemical process in use for the generation of alkaline hydrogen peroxide by the electroreduction of O₂. There is another commercial electrochemical process that generates peroxide by the electrooxidation of sulphuric acid (H₂SO₄) to peroxydisulphuric acid (H₂S₂O₈), however the process is now obsolete [Oloman, 1996].

In the Dow-Huron process, the cathode is composed of 1-3 mm graphite particles coated with a mixture of carbon black and Teflon and operated in a continuous co-current downward G/L flow at 0.1 MPa (abs) O₂ pressure, a current density ca 0.7 kA m⁻², a cell voltage of 2.4 V per cell and a temperature of ca 30 °C. This process typically produces a product peroxide solution with a NaOH/H₂O₂ weight ratio of ca 1.6-1.7, (6 %_w NaOH with 4 %_w H₂O₂) and a peroxide current efficiency of 85%. Peroxide current efficiency is defined as the percentage of the total current that goes in to generate peroxide (cf.

Appendix A). The entire plant is automated and the lifetime of the cell components is estimated at ca 3 years [Mathur and Dawe, 1999]. There is presently only one plant running on this process because of the relatively large capital investment required. For a plant producing 5 tonnes/day H_2O_2 , the cost projection is US \$500,000 for capital and US \$0.75/kg H_2O_2 for capital amortisation plus operation with a cathode life of 6 months.

The large capital investment of the Dow-Huron process is due to the relatively low current density. There is a limitation to the increase of current density because of the low oxygen mass transfer rate caused by the low solubility of O_2 in electrolyte solutions. The current density cannot be significantly increased for this process as it operates at atmospheric pressure. Also, the Dow-Huron reactor uses a mono-polar configuration that leads to a high capital cost of the bus bars and allied electrical accessories.

An alternative process has been developed at UBC that circumvents the problem of low mass transfer capacity and uses a bipolar instead of a mono-polar configuration. A high mass transfer rate is achieved by operating the process with co-current G/L flow at a superatmospheric pressure (800-1200 kPa gauge) using high gas and liquid loads. The UBC process operates with a diaphragm separator that allows some liquid convection through the diaphragm enabling the process to be run with a single electrolyte flow compared to a process running with a membrane separator that only allows ion exchange and therefore requires two different electrolytes on either side of the separator (anolyte on anode side and catholyte on cathode side). A problem arises in increasing the current density beyond about 2 kA m^{-2} . The problem is associated with the generation and removal of oxygen from the anode. Oxygen is generated on the anode due to an electrochemical reaction (Chapter 2) and inhibits electrolyte contact with the anode surface. Poor electrolyte contacting causes increased local current densities that lead to severe local heating and rapid anode corrosion. Therefore oxygen disengagement is essential for the efficient running of the UBC peroxide reactor at current densities $> 2 \text{ kA m}^{-2}$ (approx.).

To promote good contact of the electrolyte with the anode, Oloman used a perforated bipole electrochemical reactor as disclosed in U.S. patent 4,728,409. The perforations allow oxygen disengagement and more efficient contact of electrolyte with the anode. Good electrolyte contacting prevents anode corrosion and allows the perforated bipole electrochemical reactor to be run at current densities potentially up to ca 5 kA m^{-2} . Such a perforated bipole electrochemical reactor was demonstrated at UBC in 1983 with ten 0.4 m^2 cells operating at 800 kPa O_2 pressure, 60°C , 2.5 kA m^{-2} , 2 V per cell and 75 % current efficiency (H_2O_2) to give 2%_w H_2O_2 in 6%_w NaOH with a specific energy requirement of 4.2 kWh kg^{-1} . Specific energy for peroxide generation is defined as the electrical energy consumed to produce 1 kg of peroxide (cf. Appendix A). Cost projections for this process for 5 tonnes/day H_2O_2 indicate a capital cost of around US \$300,000 per tonne per day H_2O_2 (circa 1994) and operating costs of ca US \$ 0.3/kg H_2O_2 with a cathode life of 1 year [Oloman, 1996].

Development of a commercial process for alkaline peroxide generation must confront competition from the thermochemical process. The present merchant price of hydrogen peroxide is US \$0.75/kg H_2O_2 : i.e. US \$0.24/lb for 70%_w solution based on February 2003 costs [manufacturing.net].

The issues in scaling-up and commercializing the perforated bipole electrochemical reactor are discussed separately in Chapter 3.

1.4 Objective of the present work

The objective of the present work is to study the operation of the perforated bipole electrochemical reactor for the electrosynthesis of alkaline peroxide, to model the system, to scale-up to a multi-cell reactor operating at current density up to 5 kA m^{-2} and make a preliminary assessment of the commercial viability.

A broader problem definition, the consequent electrochemical process objective and proposed solution are discussed in Chapter 3.

CHAPTER 2

Background and Literature Review

Hydrogen peroxide can be generated by the electroreduction of oxygen. However there are several pathways for the electroreduction reaction. To select a suitable cathode material, it is useful to understand the reduction of oxygen in aqueous solutions.

2.1 Electroreduction of oxygen

The mechanism of oxygen electroreduction depends on many factors, including the type of cathode material, temperature and electrolyte. In general the reduction in aqueous electrolytes may proceed by two overall pathways [Yeager et al., 1996] and [Kinoshita, 1992].

2.1.1 Direct 4-electron pathway

In alkaline solutions:

In acidic solutions:

2.1.2 Peroxide 2-electron pathway

In alkaline solutions:

followed by:

and the thermochemical decomposition:

In acidic solutions:

followed by:

and the thermochemical decomposition:

The thermodynamic favourability of an electrochemical reduction reaction increases with the increasing value of the standard reduction potential (cf. Appendix A). It may be argued by observing equations (2.3) and (2.6), that since the oxygen half-cell electroreduction is thermodynamically more favourable in acidic solution ($E_e^\circ = +0.670 \text{ V vs NHE}$) than in alkaline solution ($E_e^\circ = -0.076 \text{ V vs NHE}$), peroxide should be generated in acidic instead of alkaline media. However, two factors prevent such an occurrence. These are:

- 1) The kinetics of oxygen reduction is intrinsically slow in acidic solutions as opposed to alkaline solutions [Oloman, 1996].
- 2) Relatively expensive anode materials and a high anode potential are needed to drive the complementary oxygen evolution reaction at the anode with $\text{pH} < 12$.

Therefore peroxide is most conveniently generated in alkaline media.

The direct 4-electron pathway involves a number of steps in which oxygen is reduced to OH^- or water. The 4-electron route may produce a peroxide intermediate but does not lead to peroxide in the solution phase. On the other hand, the 2-electron peroxide pathway involves peroxide species as an intermediate. These pathways are dependent on the cathode materials used. For instance the 4-electron pathway is predominant on noble-

metal electrocatalysts (e.g. Pt, Pd, Ag) and metal oxides (e.g. perovskites, pyrochlores). The 2-electron pathway appears to be predominant on most carbons, gold, mercury, most oxide covered metals (e.g. Ni, Co), and most transition-metal oxides (e.g. NiO, spinels) [Kinoshita, 1992].

In essence, the electrode materials that reduce oxygen via the peroxide pathway are the only ones leading to hydrogen peroxide accumulation in solution. The other electrode materials are not amenable to form hydrogen peroxide in solution. Comparing reactions (2.3) and (2.4), it may be observed that the reduction of perhydroxyl (HO_2^-) is thermodynamically favoured over the reduction of oxygen. This makes it appear that perhydroxyl ions, HO_2^- , may never accumulate in the solution phase. However, carbon and gold are known to be two electrodes [Kinoshita, 1992] where the HO_2^- reduction reaction (2.4) is two orders of magnitude slower than the oxygen reduction reaction (2.3) [Sudoh et al., 1985a]. This allows satisfactory current efficiencies (cf. Appendix A) for HO_2^- generation and accumulation on cathodes of graphite, carbon black and gold.

2.1.3 Effect of pH on oxygen electroreduction

To illustrate the effect of pH on the electroreduction of O_2 (reactions (2.3) and (2.6)), the exchange current density value for gold in 0.1 M KOH is compared to its value in 0.5 M H_2SO_4 as shown in Table 2.1. The higher exchange current density j_0 (cf. Appendix A) of oxygen reduction on gold in KOH as compared to H_2SO_4 solution is explained by the fact that OH^- ions allow the formation of hydrogen bonds between adjacent adsorbed O_2 and OH^- and is referred to as the joint pseudosplitting/peroxide mechanism [Kinoshita, 1992]. In essence O_2 is more easily electroreduced in alkaline solutions than in acidic solutions. A more complete review on the effect of pH on electroreduction is however beyond the scope of the present work.

Table 2.1 Standard exchange current density on gold for reactions (2.3) and (2.6) in different electrolytes [Kinoshita, 1992]

Electrode	Electrolyte	j_0 (kA m ⁻²) at 298 K
Reaction (2.3) on Au	0.1 M KOH	4 e-9
Reaction (2.6) on Au	0.5 M H ₂ SO ₄	1 e-12

Another process for peroxide generation developed at UBC [Gyenge and Oloman, 2001], showed that peroxide could be generated in acidic and alkaline solutions by the use of cationic surfactants that modify the pH on the cathode surface. The cell operation was carried out at 1000 kPa and 300 K with 0.1 M H₂SO₄ and 0.1M Na₂CO₃ respectively as acid and base electrolytes. The cationic surfactant (Aliquat 336[®], tricaprilmethylammonium chloride) at mM levels increased the standard rate constant of O₂ electroreduction to H₂O₂ (at 298 K) 15 times in Na₂CO₃ and 1900 times in H₂SO₄, to 1.8 e-6 m s⁻¹ and 9.9 e-10 m s⁻¹, respectively. Batch electrosynthesis performed at 300 A m⁻² superficial current density, with ca. 3 mM Aliquat 336[®] increased the current efficiency for peroxide from 12% to 61% (0.31 M H₂O₂) in 0.1 M Na₂CO₃ and from 14% to 55% (0.26 M H₂O₂) in 0.1 M H₂SO₄ at 298 K.

2.2 Three-dimensional (3D) or porous electrodes

Another factor that limits the efficient generation of peroxide in alkaline solutions is the oxygen solubility in the electrolyte. The low solubility of O₂ in aqueous NaOH (about 0.001 M at STP) imposes a low mass transfer limiting current density and requires the use of a 3D electrode to get a mass transfer capacity (k_{ms}) of at least 1 s⁻¹, with corresponding superficial current densities of the order of 1 kA m⁻². The current density prevailing on the actual surface is termed the real current density and that on the outer or superficial surface the superficial current density in a 3D electrode. The concept of 3D electrodes needs a special mention as these electrodes are important to electrochemical systems and the modelling of the peroxide reactor (one of the objectives of the present work) is difficult to understand without a proper background.

Three-dimensional electrodes are widely used in industry for reactions involving low mass transfer limited current densities (typically $< 1\text{e-1 kA m}^{-2}$) and/or in cases where the kinetics are slow. 3D electrodes provide a higher surface area for the reaction to occur thereby circumventing the limitations of low mass transfer limited current density or high overpotential. Very low real current densities ($< 1\text{e-1 kA m}^{-2}$) integrate to superficial current densities of $1\text{-}10\text{ kA m}^{-2}$, so that the electrolysis processes may be performed with nominal current densities of commercial magnitude and reasonable space-time yields.

The 3D electrode can be in the form of a fixed bed (e.g. reticulate, particulate or felt) or as a layered micro-porous gas diffusion electrode.

The mode of current transfer and fluid flow allows the possibility of two types of 3D electrodes:

- 1) Flow-through electrode: current parallel to fluid flow
- 2) Flow-by electrode: current perpendicular to fluid flow

2.2.1 Flow-through electrode

A flow-through electrode in one of its simplest forms consists of a porous bed of electroactive material (or the types discussed previously) through which electrolyte flows as shown by Figure 2.1.

Current is fed by a feeder positioned at the downstream end and is collected by a counterelectrode upstream of the bed. This counter electrode may be in free solution or separated from the reactant stream by a suitable separator (diaphragm or membrane). This configuration is usually preferred over the reverse situation, where the counterelectrode is situated downstream and the current feeder is upstream, because of the lower polarization obtained. In operation, current resides initially in solution at the downstream (anode in Figure 2.1) end, and progressively flows into the particulate phase in the upstream

direction until, at the feeder, all the current resides in the metal (electrode) phase (i.e. if there is no reaction on the feeder plate). Thus current is flowing simultaneously in both phases and the potentials of the electrode phase, and of the electrolyte, vary throughout the electrode thickness.

A major problem with the flow-through configuration is that attainment of both a high conversion and a uniform potential distribution is generally incompatible because the requirement of a deep electrode in the direction of current causes large voltage losses in the electrode (i.e. the bed depth is limited by the potential drop over its thickness t_b in Figure 2.1). Scale-up therefore is severely limited. To overcome these difficulties the flow-by configuration is employed.

Figure 2.1 Flow-through electrode

2.2.2 Flow-by electrode

Figure 2.2 shows a typical flow-by configuration. The vast majority of porous, gas diffusion and packed-bed electrodes in practice, utilize variations of this configuration.

The fractional conversion in this case is varied readily by altering the bed height. In essence the flow-by configuration provides the possibility of manipulating the potential distribution and the hydrodynamic conditions independently of each other. This allows the length of the reactor to be increased without affecting the potential drop in the 3D electrode. Therefore this type of configuration is more amenable to scale-up.

Figure 2.2 Flow-by electrode

One problem that is common to both flow-through and flow-by electrodes is that, if the specific reaction rate is large compared to the rate of mass transfer, then the reacting species are consumed mainly near the boundary (i.e. adjacent to the counterelectrode) of the structure and the bed is under-utilized. The ideal operating condition for such a cell is to achieve the mass transfer limiting current density over the entire thickness of the bed by ensuring that the over-potentials at the cathode feeder and separator correspond to the start and end of the limiting current plateau as shown in Figure 2.3 [Pletcher & Walsh, 1990]. The thickness of the bed should ideally conform with the mass transfer limited region and this thickness is known as the mass transfer

limited electroactive bed thickness τ_{max} . The electroactive bed thickness for pure mass transfer control has been calculated by Armstrong et al. (1968) and Masliy & Poddubny (1997). The electroactive thickness τ_{max} may be estimated by the following equations:

- a) Electrode conductivity (k_{aps}) $\gg$ Electrolyte conductivity (k_{apl})

$$\tau_{max} = \left(\frac{2 k_{apb} \Delta \eta}{n_o F k_m s C} \right)^{0.5} m \quad (2-a)$$

- b) Electrode conductivity (k_{aps}) $\approx$ Electrolyte conductivity (k_{apl})

$$\tau_{max} = \left(\frac{4 k_{apb} \Delta \eta}{n_o F k_m s C} \right)^{0.5} m \quad (2-b)$$

where k_{apb} is the effective electrolyte conductivity in the 3D electrode matrix ($S m^{-1}$), $\Delta \eta$ is the overpotential difference, $\eta_1 - \eta_2$ in Figure 2.3, n_o is the number of electrons exchanged in the reaction concerned, F the Faraday's constant ($96486 kC kmol^{-1}$), k_m is the mass transfer coefficient (ms^{-1}), s the specific electrode area (m^{-1}) and C the reactant concentration ($kmol m^{-3}$).

The effective electrolyte conductivity is calculated from the Neale and Nader equation (1973)

$$k_{apb} = \frac{2 k_{apl} \varepsilon_b h_l}{(3 - \varepsilon_b h_l)} S m^{-1} \quad (2-c)$$

where ε_b is the porosity of the 3D cathode, h_l is the liquid hold-up and k_{apl} electrolyte conductivity ($S m^{-1}$).

The mass transfer superficial limited current density $j_{L,s}$ may then be calculated from:

$$j_{L,s} = \tau_{max} n_o F k_m s C \quad kA m^{-2} \quad (2-d)$$

whereas the mass transfer real limited current density j_L is:

$$j_L = n_o F k_m C \quad kA m^{-2} \quad (2-e)$$

Equation (2-d) only applies to simple systems where the electrochemical reaction rate is mass transfer limited throughout the 3D electrode (cf. Appendix A).

For more complex systems, where both mass transfer and kinetics are of the same order of magnitude (mixed control), the electroactive bed thickness is determined by a complex interplay of electrolyte and electronic conductivities, electrode kinetics and mass transfer in porous media.

The simplest analogy to the current from electrolyte to the electrode phase in the 3D electrode is the co-current double pipe heat exchanger. In the co-current heat exchanger, heat is transferred from the hot to the cold fluid due to a temperature difference; analogously, the Faradaic current in the 3D electrode is transferred due to the electrode and electrolyte potential difference. The heat flux from hot to cold fluid decreases across the length of the heat exchanger, due to a decreased temperature difference; likewise, the Faradaic current density decreases along the thickness of the 3D electrode due to decreased potential difference between electrode and electrolyte (i.e. heat flux is analogous to Faradaic current density). However, there is a difference between the co-current double pipe heat exchanger and 3D electrode. In the exchanger, the heat flux is proportional to the temperature difference, whereas, the Faradaic current density (under kinetic control) is proportional to the potential difference between the electrode and electrolyte taken to some exponent. The exponentiation of the electrode/electrolyte potential difference complicates the problem and limits its analytical solution. The electrode design problem has to be solved numerically and this has been done in the present Thesis work (Chapter 5).

Figure 2.3 Strategy for operation of 3D electrode

2.3 Monopolar versus bipolar reactors

Another important concept is the choice of reactor configuration as regards to the arrangement of cells. When a reactor contains more than one cell, there are two possible ways of making the electrical connection:

- 1) Monopolar
- 2) Bipolar

It may be observed from Figure 2.4 that an external electrical contact exists on each electrode in the monopolar format. Moreover the anodes and the cathodes alternate and both faces of each central electrode are active with the same polarity. Monopolar connection requires a low voltage, high-current supply.

On the other hand, the bipolar reactor has only two electrical contacts, i.e. one to each of the end electrodes. The voltage distributes itself between the end electrodes of the bipole stack. Most of the potential drop in bipolar reactors occurs in the solution phase because of the high conductivity of the electrodes. Hence, if the total applied voltage is sufficient to drive current through the structure, then a potential difference equivalent to one monopolar cell voltage exists between two adjacent electrodes. The bipolar reactor has the advantage of using lower current and higher voltage. This translates into lower resistance losses in the bipolar reactor compared to the monopolar reactor. Also the bipolar system saves on capital cost of the rectifier (DC power supply) and bus bars that have to be used only on the end electrodes as opposed to being used on all electrodes in the monopolar design.

The simplicity of the bipolar format allows the configuration to be used in various technologies viz. water electrolyzers, chlor-alkali industry, fuel cells, nickel cadmium batteries, etc. [Pletcher and Walsh, 1990]. An important use of bipolar plate technology that may impact the whole world in the next decade or so is its use in fuel cells. Large stacks of fuel cells e.g. Proton exchange membrane fuel cells that combine hydrogen and

oxygen electrochemically to generate electrical power are being developed across the globe in order to replace the internal combustion engines in the automotive industry. The simplicity of the bipolar plate technology that allows compact fuel cell stacks to be constructed and be placed onboard a vehicle makes the fuel cell technology viable. On the other hand if the fuel cells were constructed in the monopolar format then the cost and the complexity of the cells would have prohibited its further study as an alternative to the internal combustion engines.

Figure 2.4 Monopolar and bipolar reactors

Bipolar electrodes however have two drawbacks:

- Current bypass through the manifold: As shown in Figure 2.4 current bypass may occur through the manifold and cause a loss in current efficiency [Burnett and Danly, 1979].
- Uneven fluid distribution between cells: As the current has the same value through each cell in a bipolar reactor therefore low liquid flow through one of the cells may cause the whole reactor to malfunction or promote secondary reactions leading to a severe loss in current efficiency (section 2.4.4.2).

Still, the potential simplicity of the design and low cost of the bipolar reactor led the UBC researchers to use the bipolar configuration.

2.4 Process development in electrosynthesis of peroxide

2.4.1 Early processes

In 1882, Traube (1882) showed for the first time that hydrogen peroxide is formed during the electroreduction of oxygen in water. More than a half century later Berl (1939) reported the formation of hydrogen peroxide in alkaline solution on a cathode of active carbon. In Berl's work the oxygen was fed near atmospheric pressure through a porous carbon cathode to react at the interface in a solution of potassium hydroxide (50 %_w). A porous diaphragm separator prevented the loss of peroxide in reactions at the anode. Solutions with up to 25 %_w of hydrogen peroxide were obtained by this method. The current density was generally high but decreased with increasing peroxide concentration. Typically, with a superficial current density of 2 to 3.5 kA m⁻², a solution with 12-15 %_w of hydrogen peroxide was prepared at a current efficiency of 70 to 80 % and a specific energy consumption of 7.5 kWh kg⁻¹ of hydrogen peroxide. However, when sodium hydroxide was used as the electrolyte, the results were not as good and the active carbon electrodes disintegrated when the peroxide concentration exceeded 1 %_w.

Berl's process was proposed for commercial peroxide generation but has never been used. Apart from the need to regenerate special cathodes, the cost of potassium hydroxide makes the process uneconomic.

Mizuno (1949) investigated the process using a cathode of active carbon and obtained the same results as Berl. Later studies of the reduction of oxygen on active carbon are described in a series of patents by Grangaard (1969a, b, c, 1970). Grangaard used a porous graphite electrode and a semi-permeable diaphragm to allow the electrolyte to flow continuously from the anode to the cathode compartment. With a superficial current density of 0.1 kA m⁻², this method produced a solution of 0.5% hydrogen

peroxide in 2% sodium hydroxide with a specific energy consumption of 3.84 kWh/kg of peroxide. However, there is no record of this process ever being used commercially [Oloman, 1986].

2.4.2 Electrolytic fluidized bed system

Oloman and Watkinson (1975) made a study of the 2 & 3-phase fluidized bed system to generate peroxide. It was found that the peroxide concentrations were too low at atmospheric pressure to be of any commercial interest. The highest superficial current densities achieved were about 0.08 kA m^{-2} , which is at least an order of magnitude lower than the values which have been achieved using other electrodes. Moreover the bed also showed a decrease in current efficiency beyond a fluidization of 5% (i.e. 5% increase in cathode bed height) possibly due to a potential distribution that was unfavourable for the accumulation of peroxide. Further work on fluidized beds for peroxide generation was therefore aborted.

2.4.3 Packed bed electrodes

Oloman and Watkinson (1976) then moved on to fixed bed electrodes involving both single and two phase flows. In this work they used a fixed bed of graphite particles as the cathode and studied the system up to a pressure of 1200 kPa (abs). The cell configuration consisted of a divided electrochemical cell fed with separate anolyte and catholyte of 1 M and 0.1 M NaOH solutions respectively, separated by a cation exchange membrane. It was seen from this work that the two-phase system with the gas flowing along with the electrolyte, performed better than the single-phase system in which the gas was dissolved in the electrolyte. In the two-phase system the electrolyte remained essentially saturated as it passed through the reactor due to the transfer of oxygen from the gas to the liquid. In addition, the mass transfer rate of oxygen in the liquid was much higher. Results were thought to be influenced by the changes in the gas and liquid distribution. The current density for cell operation was rather low (0.18 kA m^{-2}). To attain practical current densities it was realized that the two-phase system was required to be

operated under superatmospheric pressure. When the catholyte superficial velocity was $3.3 \times 10^{-4} \text{ m s}^{-1}$ the peroxide concentration reached 0.15 M at a current density of 1.2 kA m^{-2} and a current efficiency of 21% (at a pressure of 1200 kPa abs). The work in itself was not sufficient to make a commercial cell but guided further development by indicating the gas-liquid flow regimes in which such a cell could operate.

2.4.4 Trickle bed electrodes

Trickle bed electrodes have been studied for peroxide generation by various groups. Depending on the electrochemical process to be carried out, the reactor may be divided into separate cathode and anode chambers by an ion specific membrane with a catholyte and an anolyte flowing through the respective chambers or into an undivided cell using a porous insulator such as a diaphragm that uses only one electrolyte flow.

The work on peroxide generation on a trickle bed electrode using a diaphragm separator may be broadly classified into three categories:

- a) UBC cell
- b) Dow-Huron cell
- c) Other groups and the bipolar trickle tower

2.4.4.1 UBC cell

Taking a cue from their earlier work on packed bed electrodes, Oloman and Watkinson (1978, 1979) and Oloman (1979) found that hydrogen peroxide could be produced in the desired concentration if the electrolyte and gas were introduced to the reactor in the trickle flow regime. This flow regime is essentially gas continuous, or more specifically, a transition from liquid continuous to gas continuous with the liquid trickling down the electrochemical reactor bed. That is, the fluid dynamics is analogous to a thermochemical trickle bed reactor. A major difference is, however, the limitation of

effective electrode thickness in the electrochemical trickle bed reactor to a maximum of 10 mm or less in the direction of current (section 2.2.2).

Oloman and Watkinson's work involved an electrochemical reactor with a metal cathode plate, a 3 mm thick bed of 0.5 mm thick spherical graphite particles, a porous non-conducting diaphragm and a metal anode plate compressed in a sandwich as shown in Figure 2.5. The reactor was operated with a co-current flow of oxygen gas and NaOH electrolyte solution downward through a graphite bed as shown in Figure 2.5. The nature of the flow through the cathode influences the mass transfer, cell resistance and current efficiency. According to Satterfield (1975), the flow rates used in the work was in the slug flow regime (between gas continuous and liquid continuous) with liquid trickling down the bed.

The chemical reactions occurring on the cathode are those given by equations (2.3), (2.4), (2.5) plus

Reactions (2.3) and (2.4) are electrochemical reactions whereas (2.5) is a thermochemical reaction that may occur on the cathode bed catalyzed by metal contaminants in the electrolyte solution. Amongst the three electrochemical reactions (2.3), (2.4) and (2.9), reaction (2.9) is thermodynamically and kinetically the least favourable and may occur only when there is insufficient oxygen or perhydroxyl ion, (HO_2^-) in the system so that reactions (2.3) and (2.4) are not possible or reach the mass transfer limit.

The balance of the formation reaction (2.3) and reduction reaction (2.4) depends primarily on the cathode material [Yeager et al., 1964], together with the oxygen pressure, peroxide concentration and effectiveness of mass transfer.

The rate of secondary reaction (2.4) increases with increasing perhydroxyl concentration, resulting in a lower current efficiency for peroxide (Appendix A) with

increasing current density. Perhydroxyl and hydroxyl ions are also transported through the diaphragm to compete, respectively, for the following two anodic reactions:

Figure 2.5 Trickle bed electrochemical reactor [Oloman and Watkinson, 1979]

The ratio of the diffusivities of hydroxyl and perhydroxyl ions is about 4/1 so the diffusion flux is also in the same ratio. However, there is some convection through the diaphragm that adds to the peroxide losses. This convective flow is essential in the UBC cell as it maintains sufficient wetness of the diaphragm to keep the conductivity of the diaphragm high and supplies reactant (hydroxyl ions, OH^-) to the anode. The high conductivity in turn reduces the diaphragm potential drop and lowers the cell voltage, but also increases perhydroxyl loss by convection, to lower the current efficiency. Also, a low wetness of the diaphragm could be detrimental to the cell operation as it may lead to

high diaphragm resistance burnout due to increased Joule heating at high current densities ($> 3 \text{ kA m}^{-2}$).

Perhydroxyl and hydroxyl ions are also transported to the anode by migration. The main anodic reaction is the generation of oxygen from hydroxyl ions by reaction (2.11). However any perhydroxyl ions reaching the anode are also destroyed by reaction (2.10).

The influence of major operating parameters and design variables on current efficiency, peroxide yield and voltage requirements have been investigated by Oloman and Watkinson (1979) and Oloman (1979).

Oloman observed that in the cell configuration of Figure 2.5, the current density could not be increased beyond a particular value (typically about 2 kA m^{-2}) because of corrosion problems on the anode due to oxygen generation. In order to circumvent this problem Oloman (1988), as disclosed in U.S. patent 4,728,209, devised a novel type of electrochemical reactor called the perforated bipole reactor. The patent is the subject of the current Thesis work and is discussed in detail in Chapter 3.

2.4.4.2 Dow-Huron cell

McIntyre and Phillips (1982, 1983a, 1983b) devised the cell shown in Figure 2.6, which reduced the peroxide loss on the anode considerably. This cell is commercially available under the name of the Dow-Huron cell (Dow Chemical Co. and Huron Technologies Inc.) previously mentioned in Chapter 1. In the Dow-Huron cell the electrolyte trickles down through the cathode bed under gravity along with a co-current flow of excess O_2 . The mass transfer capacity is increased by the increased specific surface area of the carbon black and the hydrophobicity of the Teflon that allows the O_2 to penetrate the pores of the carbon matrix. The separator used in this reactor is also similar to the one used in the UBC cell (micro-porous polypropylene diaphragm). The diaphragm is arranged so as to allow a controlled flow of electrolyte (NaOH) from the

anode chamber to the cathode bed. This type of cell in effect imparts a convective motion to the perhydroxyl ions, HO_2^- , in a direction opposite to the diffusive and migration flux. This prevents peroxide loss at the anode [Oloman, 1996].

The Dow-Huron cell is however faced with problems. Clifford et al. (1990) and McIntyre (1995) reviewed various considerations in the scale-up of the Dow-Huron cell such as diaphragm flow control of electrolyte, IR drop in the bed, product ratio control and cell design criteria. It was realized that to operate the cell at high current efficiency, a controlled flow of electrolyte through the porous diaphragm was required on to the porous cathode bed. Too high a flow rate would cause flooding of the bed, while too low a flow rate would not provide enough wetted active sites on the carbon matrix to support a reasonable current density in the bed. The flow rate could then be controlled, simply by adjusting the anolyte hydrostatic head. However, the variation in flow rate through the diaphragm at the top and the bottom would be too large to make effective use of the whole bed. In that case the problem may be circumvented by the use of a multiple layers of the diaphragm in the bottom portion to provide a uniform flow. However the diaphragm resistance constrains the cell height to a maximum of 1 metre. So the reactor cannot be scaled up above a height of 1 metre.

Another problem with the Dow-Huron cell is that it operates near atmospheric pressure (100-130 kPa abs.). And because the oxygen solubility is low at such pressures there is a mass transfer limitation of oxygen reduction at the cathode. The oxygen mass transfer rate constrains the maximum superficial current density of the cell to less than 1 kA m^{-2} , leading to a relatively high electrode area compared to the UBC cell where the reactor may be potentially operated up to 5 kA m^{-2} . The high superficial area translates into a high capital cost for the Dow-Huron cell (Chapter 1).

Another issue dealt with in Dow-Huron reactor was the choice of cell format, i.e. either monopolar or bipolar (discussed in section 2.3). In the monopolar format as shown in Figure 2.7, differences in oxygen distribution to cells are reflected in redistribution of

current to the other cells with adequate oxygen. This primary consideration along with the design of a convenient trickle bed system led Huron to favour the monopolar format.

Figure 2.6 Dow-Huron single-cell reactor

Figure 2.7 Monopolar format of Dow-Huron reactor

2.4.4.3 Other groups and the bipolar trickle tower

Trickle bed electrochemical reactors have also been studied by Spalek and Balogh (1986, 1989a, 1989b, 1991). Spalek and Balogh (1986) provided a model for the calculation of potential and concentration gradients in trickle bed electrodes producing hydrogen peroxide. The model was similar to the one given by Oloman (1979) however it carried that work further. The model calculated the potential distribution along the current flow and hydrogen peroxide profile along the electrolyte flow. This model however neglected the potential drop in the electrode material by assuming the conductivity of the electrode material to be much higher than that of the electrolyte.

Spalek and Balogh (1989b) compared the experimental and theoretical values of electric potential in the bed for different flows of oxygen and electrolyte. The experimental results for the change in electrode potential with changing oxygen flow were in good agreement with the theoretical results. However, the results for the change in electrode potential with changing electrolyte flow were at variance with the theoretical results. The experimental results showed that increased solution flow rate made potentials more negative while the theoretical results gave reverse trends. This was probably due to the assumption in the model that the gas-liquid (G-L) and liquid-solid (L-S) interfacial areas were the same. However in reality, the G-L interfacial area is much smaller than the L-S interfacial area [Spalek and Balogh, 1989b]. Since the G-L film is the rate controlling one, the effect of reduction of oxygen transport within the trickle bed electrode due to the reduction in the gas-liquid interfacial area may outweigh the effect of the increase in the mass transport coefficients, resulting in a net decrease in the rate of the process. The current efficiency was however found to go up with the increase in solution flow rate. This was explained by the fact that since the liquid flow rate does not produce a positive shift in the electrode potential, the positive effect of the liquid flow rate on the current efficiency is just the result of a lower peroxide concentration in the solution at an increased flow rate and reduced rates of all processes that involve peroxide loss. (i.e. the reduction, decomposition and the peroxide transport to anode compartment). The potentials of the electrodes studied were found to be more positive at the outlet pressure

of 0.2 MPa (abs.) compared to atmospheric. This is due to the increased solubility of oxygen, and hence increased rate of reduction. Also there is an increase in the exit concentration of peroxide because the greatest loss of peroxide in trickle bed electrodes, due to its reduction, decreases with a positive shift in the potential.

Spalek and Balogh's reactor was similar to that of Oloman (1979); however, there is no literature evidence that Spalek and Balogh's design has been employed in a commercial cell.

Extensive work on trickle bed reactors has been done by a group of Japanese workers under Sudoh and Yamada.

Sudoh et al. (1985a, b) studied the co-current flow of oxygen and NaOH fed to the bottom and exiting at the top of a reactor. This reactor consisted of a bed of graphite particles acting as the cathode. The flow mechanism and the flow velocities were similar to that in the UBC cell. They did a model analysis of the peroxide generation that was based on mass transfer limited current density and compared their experimental results with the model. Their work also calculated the kinetics of perhydroxyl ion formation reaction (2.3) and reduction reaction (2.4) on carbon-based cathodes. The kinetic data for peroxide generation and reduction on carbon at 15 °C, due to Sudoh et al. (1985a) has been used in the modelling work in Chapter 5 of this Thesis.

More recent work by Sudoh et al. (1999, 2001a) studied the flow distribution of gas and liquid through a graphite felt cathode at room temperature (293K). They compared the co-current flow of oxygen and NaOH from bottom to top versus top to bottom of a reactor. They found that the top to the bottom approach provided higher current efficiencies for peroxide generation compared to the bottom to the top approach in a current density range of 0.1-0.8 kA m⁻². The reason for higher current efficiency in the top to bottom approach was explained by the higher wetting efficiency of the graphite felt and higher mass transfer coefficient of oxygen to graphite felt surface as opposed to the bottom to top approach. Higher current efficiency for peroxide generation in the top

to bottom flow configuration appears contrary to the present work at UBC where the bottom to top approach for operating the reactor is preferred. A high mass transfer rate of oxygen through the electrolyte to the cathode surface is possible in the bottom to top approach as opposed to the top to bottom one due to a higher mass transfer capacity in the former [Hodgson and Oloman, 1999]. However, in Sudoh et al.'s work the flow velocities ($2\text{e-}5$ - $8\text{e-}5$ m s^{-1}) of the liquid were much lower than the flow velocities in the UBC cell ($4\text{e-}3$ - $5\text{e-}3$ m s^{-1}). The low liquid flow velocities used by Sudoh et al. resulted in low a liquid hold up (ca 0.1) and wetting efficiency, leading to a significant influence on the current efficiency. In the UBC cell the liquid hold up was higher (ca. 0.6-0.8) and therefore the wetting efficiency did not have a strong effect on the current efficiency. Also the reactors in the UBC cell were operated at higher pressures (800-1200 kPa gauge) as opposed to atmospheric pressure (100 kPa abs) in Sudoh et al.'s work and therefore, the overall rate of peroxide generation was not necessarily limited by mass transfer of oxygen to the cathode surface.

Sudoh et al. (2001b) have also studied graphite felt cathodes by altering their wetting efficiency. They deposited polytetrafluoroethylene (PTFE) onto the graphite felt cathodes and varied its fraction from 0-60%_w. They found that 15 %_w PTFE provided maximum current efficiency for peroxide generation.

Yamada et al. (1998, 1999) carried out studies on a trickle bed reactor for the generation of alkaline peroxide solutions using a dual compartment cell of $5\text{e-}3$ m^2 superficial cathode area. The anode and the cathode compartment were separated by a cation exchange membrane (Nafion 117, Dupont Inc.). The anode of stainless steel web and the cathode of carbon felt, were fixed together between nickel plates as a current feeder. The feed solutions to the anode and cathode were 2M NaOH prepared using de-ionized water.

Experiments were carried out with different sources of oxygen such as air, pressure swing adsorbed (PSA) oxygen and pure oxygen. The PSA oxygen contained 95% O_2 , 5% N_2 and less than 0.01% CO_2 . According to the authors, the presence of

carbon dioxide created the problem of sodium carbonate crystallization on the cathode bed due to the common ion effect. This led to a decrease in current efficiency as result of an increased rate of perhydroxyl reduction reaction (2.4) due to the lower surface area available for reaction on the cathode bed. Also CO_2 in the solution lowers the pH of the catholyte, which increases the reduction by the peroxide reaction (2.4) and whose rate is considerably faster in acidic solutions than in alkaline solutions. Furthermore, the work investigated the liquid and oxygen supply modes. It was seen (Figure 2.8) that when the liquid and oxygen gas were supplied separately to the cathode, the current efficiency went down compared to a uniformly mixed flow of liquid and oxygen dispersed by spraying (i.e. the oxygen caused the spraying).

NaOH concentration (catholyte and anolyte): 2M

Figure 2.8 Effect of liquid-gas spraying on cell performance [Yamada et al, 1998]

Through the study of the liquid hold up effect on the current efficiency, a thin liquid layer on the carbon electrode was found to be the most desirable condition to maintain good mass transfer. This explains why the spray type supply system is more effective than the separate gas and liquid feed.

Scale-up studies were carried out on a 0.8 m^2 cell but the results were not in consonance with those obtained in a $5 \text{ e-}3 \text{ m}^2$ cell. The poor results with the 0.8 m^2 cell were probably because of the uneven distribution of the liquid in the cathode felt.

Bipolar trickle tower

Peroxide generation can also be considered in a bipolar trickle tower as shown in Figure 2.9a. Here each layer of bipolar electrode particles is separated from its neighbour by an insulating mesh. The potential distribution is non-uniform along the flow direction such that peroxide may be formed and reduced via reaction (2.3) and (2.4) respectively, and subsequently oxygen may be generated via reaction (2.10) and (2.11) on the anodic side of the bipolar electrode. It would be difficult to generate peroxide solution with high peroxide current efficiencies ($\geq 90\%$), as the peroxide losses on the anodic side of the bipolar electrode will be substantial unless the oxidation of peroxide could be suppressed by the choice of an electrocatalyst on the anodic side of the bipole.

As may be observed from Figure 2.9b, in bipolar trickle towers only a portion of the bipolar electrode is electroactive and the remaining portion, the inactive zone, does not contribute to any electrochemical reactions, as the potential ($|\phi_s - \phi_b|$) in the inactive zone is less than the critical potential, thus preventing any electrochemical reactions from taking place on the electrode. Here ϕ_s is the electrode potential and ϕ_b the electrolyte potential.

Current can also bypass through the thin electrolyte film in Figure 2.9a, and cause a loss in peroxide current efficiency. So these reactors are best suited for poorly conducting electrolytes [Pletcher and Walsh, 1990]. There is no literature that suggests this type of reactor ever being employed for peroxide generation.

Figure 2.9a Bipolar trickle tower
[Pletcher and Walsh, 1990]

Figure 2.9b Potential distribution over a
single bipolar layer of bipolar particles

In essence the UBC perforated bipole trickle bed electrochemical reactor has the novelty of making provisions for anodic gas disengagement (O_2 generated on the anode) through perforations that allows the reactor to be used at current densities exceeding 2 kA m^{-2} . High operating current density can lower the capital cost of the electrochemical reactor that could make the UBC reactor commercially viable.

2.4.5 Gas diffusion electrodes

Berl's work (discussed in section 2.3.1) was extended and comprehensive investigations were performed by a group of Czech workers (Spalek and Balogh) as reported by Bombard and Fuller (1994). Spalek and Balogh studied an electrochemical reactor with what is known as the fuel cell electrode. The properties of various types of carbonaceous materials were explored. A mathematical model of peroxide formation and diffusion was derived.

The gas diffusion electrode based reactor (Figure 2.10), also known as the E-TEK reactor, uses a gas diffusion cathode comprising layers of carbon black/Teflon mixture pasted onto a substrate of graphite cloth. Electrolyte and oxygen gas are introduced to opposite faces of the cloth. The reaction occurs on the meniscus formed by the gas, liquid and solid. The gas diffusion electrode provides a high mass transfer capacity for gas from the high specific surface of the microporous electrode matrix. The E-TEK reactor uses a cation permeable membrane as a separator because of its ability to eliminate peroxide losses to the anode. The E-TEK reactor operates at 50°C and near atmospheric pressure, with a current density up to about 2 kA m^{-2} at 2.3 V to produce 5 %_w H₂O₂ in 12 %_w NaOH at around 85% current efficiency [Oloman, 1996].

The major limitation of this work is the precipitation of sodium peroxide (Na₂O₂·8H₂O) within the cathode matrix at temperatures below 40 °C. Besides this, it is difficult to design the gas diffusion electrodes for use in free electrolyte at gradients of bottom to top hydraulic pressures equivalent to more than about 1 m of electrolyte while avoiding excessive percolation of feed gas and penetration of electrolyte to the gas plenum [Oloman, 1996].

An oxygen diffusion cathode has also been investigated in a peroxide cell by Chiang (1988). The NaOH electrolyte solution was allowed to flow by capillary action across horizontal electrodes separated by a perforated diaphragm. Air was used as a source of oxygen at the cathode and generated oxygen at the nickel anode was allowed to pass through the diaphragm into the cathode. This experimental cell produced about 1.5%_w H₂O₂ in 4%_w NaOH at a current density of 0.2 kA m^{-2} at 1.2 V per cell and a current efficiency of about 90%. However the current density was too low for the process to be of commercial interest.

To develop more economical systems, electrochemical generation of alkaline peroxide solutions has also been studied in fuel cells. Otsuka and Yamanka (1990) reported a divided fuel cell containing Nafion 117 electrolyte with Pt deposited on one of

its faces, where H_2 is oxidized and graphite or Au-mesh where O_2 is reduced to hydrogen peroxide. For an optimum 0.1 M HCl solution in contact with the cathode, the current efficiency dropped sharply from 100 to 70% during 3 h of operation [Brillas et al., 2002].

Figure 2.10 Gas diffusion electrode based reactor

Webb and McIntyre (1996) have described a divided fuel cell using a polyfluorosulphonic acid ionomer membrane between a H_2 diffusion anode and a O_2 cathode with different catalysts. This system yielded current efficiencies lower than 70%.

More recent work on alkaline peroxide generation using gas diffusion electrodes has been done by Brillas et al. (2002). In their work they used an undivided fuel cell based on hydrogen oxidation and oxygen reduction gas diffusion electrodes. The electrodes had a $3.8 \times 10^{-4} \text{ m}^2$ superficial surface area. The catalyzed hydrogen diffusion electrode was an ECC carbon cloth 10% Pt/C electrode, composed of a carbon cloth covered with a layer of PTFE and carbon black with 10% Pt. The oxygen diffusion cathode was a 'speciality for hydrogen peroxide' electrode [Brillas et al., 2002]. The diffusion electrodes used in their work had been obtained from E-TEK Inc.

Fresh KOH was used as an electrolyte as the cell performance degraded with time due to HO_2^- adsorption on the cathode. A previous study on a gas diffusion reactor with a

superficial electrode area of 0.78 e-4 m^2 cell had shown that a quasi-steady behaviour was observed when a fresh KOH solution was continuously injected through the reactor [Brillas et al., 1998].

KOH was used as an electrolyte in Brillas et al.'s work (2002) in place of the more commonly employed NaOH for two reasons:

1) KOH has higher electrolyte conductivity than NaOH for the same concentration, therefore a higher current density can be obtained.

2) NaOH causes $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ precipitation on the gas diffusion cathode at temperatures below 40°C thereby compromising its performance as has also been reported earlier in the discussion of the E-TEK reactor in the present work (and many years ago by Berl (1939)).

Current efficiencies close to 100% were achieved in the reactor due to Brillas et al. (2002) at current densities viz. 1 kA m^{-2} . The reactor shows promise of being scaled up to a larger size, however the reactor size (3.8e-4 m^2) and the peroxide concentration (maximum of 0.022M) are too small for it to be of commercial interest at present.

2.4.6 Bipolar membranes

Drackett (1994) studied a reactor using a bipolar membrane separator and a gas diffusion cathode for the generation of hydrogen peroxide. The NaOH/ H_2O_2 ratio obtained was 0.75 with a catholyte and anolyte feed of 5%_w NaOH at 1 kA m^{-2} and 4 V per cell and a current efficiency of 86%. A low NaOH/ H_2O_2 ratio is obtained in this process because the hydrogen ion generated by water splitting in the bipolar membrane migrates to the cathode chamber and neutralizes the hydroxide produced at the cathode. A high cell voltage and poor membrane stability (< 3 months) prevented the reactor from being commercialised. Future developments in bipolar membrane technology may make this an attractive process.

Having reviewed the mechanism of peroxide generation and various reactor configurations that have been investigated over the years, the problem and objectives of the present Thesis work may now be discussed.

CHAPTER 3

Problem Definition, Objective and Proposed Solution

Most bipolar electrodes are solid, typically, metallic elements. That is, such electrodes are constructed so that electrolyte cannot pass through them, other than perhaps through the electrolyte inlet and outlet manifolds. In some processes, one of the disadvantages of solid bipolar electrodes is the accumulation of gas on them. Such gas accumulation limits the maximum superficial current density that can be applied to the electrodes. Furthermore, gas accumulation causes non-uniform current distribution and can result in corrosion (particularly of the anode) as well as overheating, loss of selectivity and loss of energy efficiency. To circumvent this problem Oloman (1988) patented an idea of enabling the gas disengagement to occur from a bipolar anode, by perforating the electrodes of the bipolar reactor. The novel perforated bipole electrochemical reactor is the primary subject of study in the current Thesis work and is discussed in more detail in the following section.

3.1 Perforated bipole electrochemical reactor

Oloman worked with a perforated bipolar electrochemical reactor as disclosed in the U.S. patent 4,728,409, for the generation of alkaline peroxide solutions by the electro-reduction of oxygen. A description of the bipolar electrochemical reactor is given here and the electrochemical reactor is shown in the Figure 3.1 below:

Figure 3.1 Perforated bipole electrochemical reactor

This is a multi-cell, parallel plate, “filter press” type continuous reactor. Each electrolytic cell comprises, in a spaced apart relationship, an anode and a cathode. Inlets are provided at the bottom for supplying an aqueous electrolyte solution and oxygen gas in the cathode mass, and outlets are provided at the top to remove alkaline peroxide solution and excess oxygen. The graphite felt cathode bed is typically compressed to about 3 mm between the cathode feeder plate and the separator. The separator is a diaphragm made of porous material such as polypropylene or polyethylene. Facing the other side of the separator is the counter electrode (anode). The perforated bipole element is anode on the right hand side and cathode feeder on the left hand side. The whole assembly is tightly packed so that resistance losses are minimized. The bipole element in this reactor is perforated, with holes typically of the diameter from 0.4 mm to 1.6 mm occupying about 1 to 5% of the electrode surface area. The perforations are evenly distributed over the bipole plate.

An aqueous alkaline solution of caustic soda and oxygen gas are fed from the bottom co-currently. Oxygen is reduced to perhydroxyl ion, HO_2^- on the graphite felt surface by reaction (2.3) and perhydroxyl ions, HO_2^- , are reduced to hydroxyl ions, OH^- ,

by reaction (2.4). Oxygen generated on the anode via reactions (2.10) and (2.11), is supposed to pass through the bipole perforations into the adjacent cathode.

3.2 Previous work on perforated bipole electrochemical reactor

Perforated bipole electrochemical reactors have been studied previously by Sudoh et al. (1985c, 1988). The reactors used the flow-through configuration (section 2.2.1) and the aim of the perforations was to allow the electrolyte to flow from one cell to another. In their work Sudoh et al. used a flow-through graphite electrode for the generation of bromine [Sudoh et al., 1985c] and degradation of phenol [Sudoh et al., 1988]. The reactors used were identical in both studies. The reactor was modelled based on an equivalent circuit accounting for the Faradaic currents on the bipolar graphite electrode and the bypass current through the perforations. The model was trivial as both the anode and cathodes were planar.

Experiments on bromine generation were studied under two different flow regimes, namely, continuous-flow (counter current gas-liquid) and trickle flow. It was found that in the continuous flow regime increasing the gas velocity reduced the energy consumption for bromine production. However, in the trickle flow regime the liquid velocity did not influence the energy consumption for bromine generation up to a velocity of 0.9 cm s^{-1} [Sudoh et al., 1985c]

In Sudoh et al.'s (1988) experimental work on phenol degradation, hydrogen peroxide was generated on the cathode and phenol oxidised on the anode to reduce the COD (chemical oxygen demand) of the organic compounds in a flow-through electrochemical reactor. The work related the effect of potential difference on the opposite faces of the bipolar electrode on the COD current efficiency through the contributions of the currents of phenol oxidation and oxygen reduction to the total current.

3.3 Problem Definition

The capital costs of electrochemical reactors are approximately directly proportional to the superficial electrode area. Therefore a good way of reducing the capital cost is to lower the superficial electrode area. This may be done by working at increased superficial current densities. In systems that are mass transfer limited and the mass transfer limited current density is low ($< 0.1 \text{ kA m}^{-2}$), a 3D electrode is required to run the electrochemical reactor at high superficial current densities ($1\text{-}10 \text{ kA m}^{-2}$ -Chapter 2). In the case of gas generating electrodes, increased superficial current densities causes the added problem of gas disengagement. One way to circumvent this problem in the bipolar reactor is to provide perforations in the bipole element that disengage the gas generated there, as had been proposed by Oloman (1988) in US patent 4,728,409. Gas disengagement is a problem mostly with the cathode/diaphragm/anode peroxide cell (UBC) design and less so with other designs.

It was also seen from Oloman's work (1988) that higher current densities are achievable with the perforated plate bipole element as compared to non-perforated bipole anode. This is due to the ease of gas disengagement that results in a more uniform local current density on the anode surface of the bipole and less severe corrosion of perforated anodes as opposed to solid anodes. Or in other words, the perforations prevent gas accumulation on the anode surface of the bipole, which if allowed to occur would cause maldistribution of current, and high cell voltages due to the increased resistance of the electrolyte path.

The perforations (or holes) in the bipolar electrode however have one important drawback. Any electrolyte present in a hole represents a conductive path that may cause a current short through the bipolar electrode. That is, current will bypass the cell without being involved in any electrochemical reaction, thereby leading to a loss of current efficiency. In order to scale-up a perforated bipole electrochemical reactor, it is important to be able establish the mechanism by which current bypass occurs through the perforations. The mechanism of current bypass is an interplay between various factors

such as the bipole anode and separator (diaphragm) materials together with the perforation size and coverage. The current bypass mechanism will become clearer when the modelling of the two-cell electrochemical reactor is discussed (Chapter 5).

Previous unreported experimental work with a 5 cell, 20 amp. perforated bipolar reactor (i.e. electrode dimensions 25 mm wide by 150 mm long by 3.2 mm thick) showed efficient operation (e.g. 78 % current efficiency) at superficial current densities up to 2.5 kA m^{-2} [Oloman, 1986]. However several attempts to scale-up these results to larger electrodes (200 Amperes on 50 mm by 800 mm electrodes) and higher current densities were unsuccessful. A major problem in these scale-up attempts was an inadequate understanding of the design of the novel perforated bipolar system.

Another problem that is critical to the design of the perforated bipole electrochemical reactor is the choice of diaphragm or separator material. In an undivided flow cell such as the UBC reactor, where there is only one electrolyte flow (as opposed to an ion exchange membrane cell with separate catholyte and anolyte flow), wetting of the counter-electrode (anode in the present work) is essential for the efficient operation of the reactor. The diaphragm material should be hydrophilic so as to allow electrolyte wetting of the anode while also suppressing the loss of the product (perhydroxyl ions, HO_2^-) generated on the cathode via reaction (2.3) due to a reverse reaction on the anode via reaction (2.10).

Poor wetting of the anode would result in maldistribution of current on the anode that could lead to severe heating and diaphragm burn out, causing the cell to short circuit. Also inadequate diaphragm wetting would give a high IR drop through the diaphragm that would increase cell voltage, translating into increased specific energy for peroxide generation (Appendix A).

Another essential feature of the diaphragm is that it should be stable in strong acidic or basic solutions (viz. 1 & 2 M NaOH in present work) at temperatures up to 80°C (resulting from Joule heating in a practical reactor).

It may be inferred from the above that more work is required to understand the design features of the perforated bipole reactor in order to have a commercially viable unit. Also, the development of a perforated bipolar reactor would be helped by a model, which could point to improved configurations and direct the experimental program aimed at scaling-up the reactor.

As described in the following section, the objective of the present Thesis is defined by the need for an improved understanding of the perforated bipole electrochemical reactor.

3.4 Objective

The original objective of the Thesis was to scale-up the reactor from the bench scale to a commercial scale reactor at 5 kA m^{-2} . The scale-up was to be achieved by working on three different size reactors that have been categorized according to the dimensions of the active or superficial electrode area as:

- 1) Small reactor (120 mm long by 25 mm wide)
- 2) Medium reactor (630 mm long by 40 mm wide)
- 3) Large (i.e. commercial) reactor (1800 mm long by 250 mm wide)

The plan was to achieve reasonably high current efficiencies (70-75%) and low specific energies (ca $4 \text{ kWh/kg H}_2\text{O}_2$) with current densities up to 5 kA m^{-2} on a 10-cell commercial size reactor so that it might compete with the existing thermochemical process for generating hydrogen peroxide by the autooxidation of anthraquinols [Oloman, 1996]. Objectives 1 and 2 have been met, but objective 3 was not achieved largely due to the non-availability of a good diaphragm material in the early stages of the work, and other experimental difficulties.

The goal of scaling up required understanding the perforated bipole electrochemical reactor from four standpoints:

- 1) The mechanism of current bypass in the perforated bipoles. For this purpose it was considered important to establish a reactor model to guide the experimental work.
- 2) Based on (1), the selection of the perforation specifications for operation up to 5 kA m^{-2} .
- 3) Selection of materials (anode, cathode and separator) for efficient operation of the reactor at current densities up to 5 kA m^{-2} .
- 4) The dependence of gas and liquid distribution in the cathodes on the manifold design, on the size and shape of the cathodes and on the number of cells in the reactor.

The following strategy was employed to seek a solution to these problems.

3.5 Proposed Solution

The solution to the Thesis problem has been carried out in the following steps:

- 1) Model a single-cell monopole electrochemical reactor for the generation of hydrogen peroxide.
- 2) Model the two-cell bipole reactor to see the effect of perforation size and coverage in the bipolar electrodes.

- 3) Select anode, cathode and separator materials for the reactor based on a better understanding of the mechanism of oxygen disengagement through the cell and experimental study on the materials. This point will be discussed in Chapter 4.
- 4) Carry out factorial runs with one, two and four cells in the small bipolar electrochemical reactor.
- 5) Compare the results of the model to the factorial run on the small reactor.
- 6) Scale-up the reactor based on dimensional similitude and modelling.
- 7) Scale-up the reactor from small to medium size using different flow configurations on the cathode bed and the anode.
- 8) Carry out factorial runs with two cells in the medium bipolar electrochemical reactor and do experiments with four cells to validate the model.
- 9) Make a conceptual design and cost estimate for alkaline peroxide production in a full-scale cell based on a perforated bipole electrochemical reactor.

CHAPTER 4

Experimental Methods, Apparatus & Materials

4.1 Process flow diagram

Figure 4.1a shows the process flow diagram used in the present work for the electrosynthesis of hydrogen peroxide. Oxygen from an O₂ cylinder and NaOH from NaOH tank, after passing through individual rotameters, join at a tee, and are fed to the bottom of the electrochemical reactor. The product peroxide in NaOH solution and excess oxygen are withdrawn from the top of the reactor and flow through a cooler and a pressure control valve (PC) into the peroxide product tank. Peroxide solution is withdrawn from the sample point and analyzed for peroxide concentration. Excess O₂ is vented in the gas-liquid separator. The latter is a packed bed of graphite felt where excess oxygen and peroxide solution are separated from each other. The cooler is provided to bring down the temperature of the product peroxide, as hot peroxide solution may decompose at a higher rate due to reaction (2.5). There is a thermometer at the exit of the reactor to monitor the temperature of the product. Power is supplied in the galvanostatic mode via the DC supply that provides constant current to the reactor. The voltage is monitored across the positive and negative terminals of the reactor using a voltmeter (V).

A pressure control valve (PC) is provided to increase the back pressure of the process fluid (O₂, H₂O and NaOH) at the exit of the reactor. Inlet and outlet pressure gauges are provided to monitor the reactor pressure. Pressure in the reactor is raised to increase the solubility of O₂ in NaOH solution. Increased oxygen solubility loosens the oxygen transfer constraint and allows the process to be operated at higher current densities ($> 1 \text{ kA m}^{-2}$).

Figure 4.1a Process flow diagram

Photographs of the DC power supply, gas-liquid separator, feed (NaOH solution) tank, peroxide solution tank and pressure control valve are shown in Figures 4.1b to 4.1e, respectively.

Figure 4.1b DC power supply

Figure 4.1c Gas-liquid separator

Figure 4.1d Feed and product tank

Figure 4.1e Pressure control valve

4.2 Reactor configuration

Experiments were carried out on two different reactor sizes (cf. Figure 4.2a) to see the effect of scale-up:

- 1) Small reactor (120 mm long by 25 mm wide and 3.2 mm thick cathode)
- 2) Medium reactor (630 mm long by 40 mm wide and 3.2 mm thick cathode)

The two reactors employed in the present work have a similar configuration. Figure 4.3 shows a single-cell reactor assembly.

Figure 4.2a Small and medium reactor (not to scale)

Figure 4.2b Medium reactor (assembly)

It may be seen from Figure 4.3 that the graphite felt cathode (5) is fitted into the Durabla (asbestos based) gasket (4) followed by a separator (diaphragm (6)), nickel mesh anode (7), perforated grafoil anode (8) and a dummy anode (9) fitted between the feeder cathode (3) and feeder anode (10). The dummy anode is electronically shorted to the feeder anode and allows the oxygen generated at the end anode to disengage from the anode and leave the reactor. The whole assembly is tightly fitted between two stainless steel plates (1) and (12) and insulated from the feeder plates (3 & 10) using Durabla gaskets (2 & 11) to form a filter press type of cell. Current is supplied to the reactor through the stainless steel (S.S.) current feeders (3 & 10) backed with copper plates on the outside of the of S.S. plates. O_2 , NaOH and H_2O enter the cell through the bottom as shown in Figure 4.3 and the product peroxide in NaOH with excess O_2 leave the reactor from the top.

Figure 4.3 Single-cell reactor assembly

The reactor of Figure 4.3 has only one cell; however, multiple cells are required in a commercial reactor. The multi-cell reactor could be operated in a monopolar or a bipolar mode. Based on the discussion in Chapter 2, reactors with bipolar electrodes were chosen for the present work. The simplest of these is a two-cell bipolar reactor which is shown in Figure 4.4 and forms the basis for the modelling work (Chapter 5).

1, 12	- Stainless steel cell body	7	- Anode (nickel mesh)
2, 4	- Durabla gasket	8	- Perforated bipolar electrode (grafoil)
3, 11	- Copper/S.S. current feeder	9	- Perforated anode
5	- Graphite felt (3.2 mm thick)	10	- Dummy anode (nickel mesh)
6	- Diaphragm (microporous polypropylene)		

Figure 4.4 Two-cell reactor assembly

The two-cell assembly is similar to the single-cell assembly of Figure 4.3, except that the two cells are adjacent to one another in series. The central perforated Grafoil sheet (8) is a bipolar electrode. It behaves as an anode on one side and a cathode feeder on the other, and allows oxygen gas generated on the anode (7) to flow into the adjacent cathode (5).

To better comprehend the reactor, it is useful to discuss the basis for selection of the materials for the anode, cathode and cell separator.

4.2.1 Anode selection

Selection of the anode material and configuration is the most critical feature in the design of the perforated bipole electrochemical reactor shown in Figure 4.4. This selection may be understood by studying the mechanism of oxygen generation and disengagement at the anode. Oxygen is generated at the anode due to reactions (2.10) and (2.11). This oxygen has to be disengaged from the anode surface before it has the opportunity to obscure the surface. Perforations are provided in the anode to disengage the oxygen into the adjacent cathode (Figure 4.3) or through the dummy anode (9) shown in Figure 4.4.

The oxygen generation rate is proportional to the current density. With an increase in current density, oxygen must be disengaged at a higher rate to prevent high local current densities. High local current density may cause severe anode corrosion and, in the case of bipolar electrodes, a loss in current efficiency (Chapter 5). Also very high current densities ($> 4 \text{ kA m}^{-2}$) would lead to high local temperatures causing the diaphragm to burn out and the cell to short circuit. Cell burn-out may be prevented by providing more holes or perforations in the anode, however, this would lead to higher current bypass through the perforations and a loss in current efficiency. A better method for preventing cell burn-out is to increase the surface area of the anode for current to transfer, so that in the case of increased oxygen generation, there is sufficient surface available for the electrolyte to conduct the current to the anode. A high surface area may be provided by 3D nickel in the form of a mesh (7) or a porous layer as an anode. The thickness and porosity of the nickel anode is critical to the whole cell set up. The choice of nickel anode is investigated further in Chapter 6. The perforated grafoil sheet (8) is placed adjacent to the nickel mesh anode (7). The two together serve as the anode in the reactor.

Grafoil has been chosen as the bipole material for two reasons:

- 1) The required perforations are easily made in the laboratory by punching the soft material.
- 2) In a multi-cell system each intermediate electrode is a bipolar electrode. One side is the anode and the other the cathode feeder. Since peroxide can be generated efficiently only on two known materials (gold and graphite (cf. section 2.0)), it is preferable to provide a cathode feeder surface, whose kinetics favour the peroxide generation reaction (2.3) over the peroxide reduction reaction (2.4), to be placed adjacent to the graphite felt cathode bed (5). This arrangement allows peroxide to be produced rather than to be destroyed by any residual Faradaic current on the cathode feeder.

Various combinations of anodes were tried in experimental runs on the small single-cell reactor. These were:

- 1) Grafoil & porous nickel (plasma sprayed nickel on nickel mesh)
Plasma sprayed nickel on nickel mesh was tried as it was expected to yield an increased surface area and lower porosity anode compared to a plain nickel mesh anode. The porosity of the nickel mesh could play a significant role in the mechanism of the gas disengagement and current exchange at the anode.
- 2) Grafoil & nickel mesh
 - a) Nickel mesh (40) (40 meshes per inch)
 - b) Nickel mesh (50) (50 meshes per inch)
 - c) Nickel mesh (100) (100 meshes per inch)
 - d) Nickel mesh (100) coated with porous nickel (electroless nickel deposited on nickel mesh)
- 3) Grafoil & stainless steel (SS) mesh
 - a) SS mesh (200) (200 meshes per inch)
 - b) SS mesh (200) coated with porous nickel (electroless nickel deposited on nickel mesh)

- 4) Raney nickel sprayed anode on stainless steel plate
- a) 0.5 mm diameter perforations with 5% perforation area
 - b) 0.5 mm diameter perforations with 1.6% perforation area

For reasons similar to that given in item 1, Raney nickel sprayed on stainless steel plate was also tried.

From the combinations listed above, the anode selected in the present work was the combination of Grafoil and nickel mesh (100) as this gave the best results and could be easily fabricated in the laboratory (cf. Chapter 6). Nickel mesh (100) was purchased from Argus Inc. of Virginia and grafoil (1.6 mm thick with stainless steel insert) from Union Carbide (New Jersey). Nickel mesh (100) and Grafoil are shown in Figure 4.5.

Grafoil sheets were punched with perforations having diameter ranging from 0.8 mm to 1.6 mm with 1 to 4% perforated area (a.k.a. coverage). These perforations were uniformly distributed on the electroactive area of the Grafoil sheet. The electroactive area is the area where the Grafoil contacts the graphite felt cathode and the nickel mesh anode.

The perforation area may be defined as:

$$\text{Perforation area (coverage)} = \frac{\text{Total area of perforations}}{\text{Superficial area of active bipole}} \quad (4.1)$$

Other types of novel anode material and configurations were also tried for peroxide generation on the perforated bipole electrochemical reactor. These are described below and the results for the experiments conducted on them discussed in Chapter 6.

Figure 4.5 Nickel mesh (100) and Grafoil (Anode materials)

4.2.1.1 NiCo_2O_4 electrodes

NiCo_2O_4 anodes were prepared using the methodology described by Carapuco et al. (1990), which involves depositing several layers of cobalt nickel oxide on a nickel mesh (100 mesh per inch). The NiCo_2O_4 electrode was then used in conjunction with a perforated Grafoil sheet to serve jointly as an anode.

A strip of nickel mesh (100), 245 mm by 50 mm in size, was first sand blasted then degreased with acetone and finally washed with 10%_w nitric acid. After cleaning, the sheet was preheated in a furnace at a temperature of 300 °C for five minutes.

A solution of nickel nitrate (0.3 M) and cobalt nitrate (0.6 M) was prepared by dissolving 29.1 grams of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 58.2 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 200 ml of distilled water. Each oxide layer was obtained by dipping the pre-treated nickel mesh into this solution of nitrates, followed by a heating stage of four minutes at 250 °C, in order to completely convert the nitrates to NiCo_2O_4 spinel oxide. This process was repeated until the whole nickel mesh was completely covered with a spinel layer. It took four such coating steps to complete the process.

The anodically active surface (120 mm by 25 mm) of the nickel mesh was masked with tape and then a silicone sealant was applied to the remaining portion of the nickel mesh. The mesh was then pressed between two smooth plates and the sealant was allowed to dry for 24 hours. The masking tape was then removed and the nickel mesh was ready for use as an anode in conjunction with the perforated Grafoil sheet.

4.2.1.2 Exploring the possibility of a novel bipole

Two different experiments were also conducted on a novel bipole electrode. The aim here was to completely eliminate the current bypass through the perforations. Current bypass as will be shown in Chapter 5, occurs due to the electrolyte present in the perforations. This electrolyte allows a current path alternate to the Faradaic one. In other words, the current that passes through the perforations is lost in the sense that it does not contribute to doing any electrochemical work. However, the perforations are essential for the disengagement of oxygen. So an ideal perforation would be one that allows the gas to disengage but not the liquid to pass through. With the intent of realizing such an electrode an experiment was carried out by placing a porous polytetrafluoroethylene (PTFE) sheet between two strips of perforated Grafoil (with 2 % perforation coverage). The PTFE

sheets have the trade name Zitex A115 and were obtained from St. Gobain performance plastics, New Jersey.

The two sheets of Grafoil with the PTFE insert in the middle together comprised the bipolar electrode. The results suggested that some current was still bypassing through the perforations. Current bypassed because the liquid was able to flow through the pores in the PTFE sheet providing an electrical path. When the reactor was dismantled after running an experiment, the PTFE sheet was found to be completely wet. After trying several such configurations a more satisfactory electrode was arrived at, one that was able to significantly reduce current bypass in the reactor (Figure 4.6). This bipolar electrode used three sheets of perforated Grafoil and two sheets of PTFE as shown in Figure 4.6. The perforations in the central Grafoil strip were filled with polystyrene beads, which provided a kind of packing that allowed the gas to disengage while at the same time preventing a liquid path from forming. Also the perforations in the three Grafoil strips were aligned during assembly.

Figure 4.6 Novel bipolar electrode

4.2.2 Diaphragm selection

The diaphragm is a critical and sensitive component of the reactor. The diaphragm or separator (6) as shown in Figures 4.3 and 4.4 is used for two purposes:

- 1) In a filter press type of cell (Figure 4.3) it prevents an electrical short circuit between the anode and cathode.
- 2) Perhydroxyl, HO_2^- and hydroxyl ions, OH^- can diffuse, migrate and convect to the anode. The selection of diaphragm should be such that it suppresses the transport of the perhydroxyl ions, HO_2^- to the anode while allowing sufficient transport of OH^- . The ratio of diffusion coefficient of perhydroxyl ions, HO_2^- to hydroxyl ions, OH^- is about 4 to 1 [Oloman, 1996]. The convective transport is dependent on the thickness, porosity and tortuosity of the diaphragm. The thicker, more tortuous and less porous the diaphragm, the lower the convective flux. However increased thickness and tortuosity and decreased porosity cause an increase in the electrical resistance of the diaphragm with relatively higher specific energies for peroxide generation. Therefore the ideal diaphragm thickness/porosity/tortuosity is a trade off between convective electrolyte flow and diaphragm conductivity. In the past microporous polypropylene diaphragms have been demonstrated to be a candidate separator material.

Previous experience at UBC has identified polypropylene as an acceptable diaphragm material. A variety of polypropylene diaphragms have been investigated in the present work and are discussed in Chapter 6. Several tests with different diaphragm materials listed in Table 4.1 are described in Chapter 6.

Table 4.1 Diaphragm properties (polypropylene)

Source: SCIMAT Ltd. of UK and supplied by Crane & Co., New Jersey

Separator type	Mean thickness (μm)	Basis weight (g m^{-2})	Ion exchange capacity (meq g m^{-1})	Electrolyte absorption* (g m^{-2})	Wicking rate 600 sec * (mm)
700/20	150	45 ± 5	0.6	> 140	> 70
700/25	220	72 ± 3.5	0.8	> 140	> 50
700/28	285	85 ± 10	0.6	> 190	> 50
700/29	115	38 ± 5	0.6	> 120	> 70
700/74	180	60 ± 5	0.8	> 75	> 75

* Measured in 30 % KOH @ 24 °C

Microporous polyethylene diaphragms were also investigated as a diaphragm material and results for scaling-up the perforated bipole electrochemical reactor are discussed in Chapter 6.

Table 4.2 Diaphragm properties (micro-porous polyethylene)

Source: DSM Solutech of Heerlen, Netherlands.

Separator type	Mean thickness (μm)	Basis weight (g m^{-2})	Ion exchange capacity (meq g m^{-1})	Mean Pore size (μm)	Porosity %	Electrical resistance* $\Omega \text{ m}^2$
SOLUPOR E075-9H01A	35	9	1.1	< 0.06	74	$< 1.5\text{e-}4$
SOLUPOR E075-9H06A	39	9	1.1	0.6	76	$< 1.5\text{e-}4$

* Measured in 30 % KOH @ 24 °C

4.2.3 Cathode selection

The choice and the nature of the cathode material is central to the modelling and operation of the reactor. According to section 2.1.2, peroxide can only be generated on materials such as carbon (most carbons, graphite), gold and mercury, most oxide covered metals (e.g. Ni, Co), and most transition-metal oxides (e.g. NiO, spinels). However, the peroxide reduction reaction (2.4) is relatively fast on all of these materials except carbon and gold (Chapter 2). In practicality, one is left with the choice of carbon as the only material on which peroxide at any useful concentrations ($> 0.1\%_w$) could be generated.

There are many forms of 3D carbon that could be used as the cathode material. Past experience at UBC with the following carbons, e.g. active carbon, crushed petroleum graphite, carbon black, reticulated carbon and carbon fibre mat or felt has shown carbon fibre felt to be superior to the other materials. This carbon fibre felt is in the form of graphite felt and was chosen as the cathode material because of its high porosity (ca. 95% uncompressed) and surface area per unit volume (ca. $2 \times 10^4 \text{ m}^{-1}$) together with the ease of fabricating large electrodes (i.e. $> 0.01 \text{ m}^2$ superficial area) from commercially available felts. Graphite felts from different sources (companies) provided more or less similar current efficiencies when the experimental runs were carried out on small single-cell reactor. In the medium-sized reactor it was found that material from Metaullics Systems Inc. (previously Carborundum), Sanborn, NY gave the highest current efficiencies. The properties of the graphite felt from Metaullics Systems Inc are listed in Table 4.3. In the present work the graphite felts could be characterized as old and new. Both graphite felts were obtained from Metaullics Systems Inc.

Table 4.3 shows that uncompressed graphite felt has a high porosity (95%) and low conductivity (10 S m^{-1}), but when compressed to 3.2 mm (small cell) the conductivity (39.2 S m^{-1}) increases and the porosity is lowered (90%).

The cost of graphite felt obtained from Metaullics systems Inc. is US \$ 50/m².

Another material that could be considered for the cathode is reticulated vitreous carbon. However, the high costs (\$150- \$300 /m²), mechanically fragile nature and lower specific surface area (ca. 200 m⁻¹) of this material made it less desirable for the present purpose.

Table 4.3 Cathode properties

Source: (Type Grade GF, Metaullics Systems Inc.)

Property	Value	Source
Initial porosity, ϵ_0	0.95	[Oloman et al., 1991]
Mean fibre diameter (μm), d_f	20	idem
Fibre density (kg m^{-3})	1500	idem
Graphitization ($^{\circ}\text{C hr}^{-1}$)	2400/2	idem
Carbon content (%)	99	idem
Uncompressed thickness (mm), t_0		
Small sized reactor	6.4	measured
Medium sized reactor	8.2	measured
Compressed thickness (mm), t		
Small sized reactor	3.2	measured
Medium sized reactor	3.2	measured
Compressed porosity, ϵ		$\epsilon = 1 - t_0(1 - \epsilon_0)/t$
Small sized reactor	0.90	
Medium sized reactor	0.87	
Compressed specific surface area (m^{-1}), s		$s = 4(1 - \epsilon)/d_f$
Small sized reactor	20000	
Medium sized reactor	26000	
Electronic conductivity of compressed matrix (S m^{-1}), k_{aps}		$k_{\text{aps}} = 10 + 2800(1 - \epsilon/\epsilon_0)^{1.55}$ [Oloman et al., 1991]
Small sized reactor	39.2	
Medium sized reactor	70.5	

4.3 Continuous 'flow-by' cells

As discussed previously in Chapter 2, continuous flow-by cells (Figures 4.3 & 4.4) have been employed in the present work with two different sized cells:

- a) Small cell (120 mm length by 25 mm width)
- b) Medium cell (630 mm length by 40 mm width)

4.3.1 Small cell cathode configuration

The cathode configuration shown in Figures 4.7a & b was used in the small cell reactor. The graphite felt was obtained from Metaullics Systems Inc. The felts were prepared by placing them in 5% nitric acid for 24 hours to remove any metal ion contaminants. A wetting agent, Makon-12 (0.001-0.02%_w) was added to the nitric acid solution to make the felt wettable. The graphite felt was then embedded between the two Durabla gaskets. The graphite felt together with the gaskets were compressed in the cell to reduce the felt thickness from 6.4 mm to 3.2 mm. The edges of the graphite felt hanging out of the gasket slots were scraped off with a brush to allow the felt to fit the slots.

The porosity of the graphite felt decreased from 95% to 90% whereas the conductivity increased from 10 S m^{-1} to 39.2 S m^{-1} due to the felt compression (Table 4.3). The superficial surface area of the felt was 32 e-4 m^2 .

The cell assembly was uniformly compressed using a torque wrench at ca 50 lb-ft on each of the 8, 1/4" diameter stainless steel bolts.

Figure 4.7a Small cell cathode

Figure 4.7b Cathode configuration (small cell: dimensions in mm)

4.3.2 Medium cell cathode configuration

The cathode configuration shown in Figures 4.8a & b was used in the medium cell reactor. The graphite felt was from Metallurgical Systems Inc. and felt preparation was similar to that in the small cell cathode (cf. section 4.3.1). The graphite felt was embedded between the two Durabla gaskets in a manner similar to the small cell cathode but the felt shape is as shown in Figures 4.8a & b. The graphite felt together with the gaskets were compressed in the cell to lower the felt thickness from 8.2 mm to 3.2 mm. Again, the edges of the graphite felt hanging out of the gasket slots were scraped off with a brush to allow the felt to fit the slots.

The porosity of the graphite felt decreased from 95% to 87% whereas the conductivity increased from 10 S m^{-1} to 70.5 S m^{-1} due to felt compression (Table 4.3). The superficial surface area of the felt was 196 e-4 m^2 .

The cell assembly was uniformly compressed using a torque wrench at ca 50 lb-ft on each of 24, 3/8" diameter stainless steel bolts (cf. Figure 4.8b).

Figure 4.8a Medium cell cathode

Figure 4.8b Cathode configuration (medium cell: dimensions in mm)

4.4 Experimental set up for observing gas and liquid flow distributions

Other than the set up shown in Figure 4.1a for peroxide generation, experiments were also done on the graphite felt cathodes of different sizes (small and medium) to assess the gas and liquid flow distribution. The experimental set up for the reactor is shown in Figure 4.9a.

Figure 4.9a Set up for observing gas and liquid flow distributions

The graphite felt cathode was cut into two different sizes for the small (Figure 4.7b) and medium (Figure 4.8b) reactors. The felts were placed between the gaskets and sandwiched between two transparent Perspex sheets as shown for example in Figure 4.9b. Flow visualization experiments were conducted on each set up through the transparent Perspex sheet. Oxygen and water were fed through the bottom of the cell and withdrawn from the top. The gas and liquid flow observations and inferences drawn from them are discussed in detail in Chapter 6.

Figure 4.9b Flow visualization set up

4.5 Additives

Various additives are used in the NaOH feed solution to prevent the decomposition of peroxide and promote wetting of the diaphragm and graphite felt cathodes.

4.5.1 Wetting agents

Wetting agents were added to the reactor feed as a standard practice to keep the diaphragm (polypropylene or polyethylene separator) wetted by the electrolyte. The usual addition was 0.002%_w of Makon NF12, a low foaming polyoxyethylene alcohol from Stepan Chemical Co. This wetting agent has a low toxicity and should be acceptable in pulp bleaching.

4.5.2 Complexing agents

Previous studies at UBC have shown that the presence of trace amounts of iron, manganese and other transition metals in the reactor feed cause an increased reactor voltage and also a decreased current efficiency for peroxide.

Complexing agents are added to the feed to suppress the loss of current efficiency. These complexing agents chelate the trace metal ions in the solution and prevent the loss of peroxide.

DTPA (diethylenetriaminepentaacetic acid, sodium salt) in the concentration range 0.01-0.2%_w was added to the reactor feed and is typically available under the trade name "Kalex Penta" from Hart Chemicals, Toronto.

4.6 Hydrogen peroxide analysis

Alkaline peroxide solution was withdrawn for a minute from the sample point shown in Figure 4.1a into a measuring cylinder. A 4 ml pipette then used to take the peroxide solution from the measuring cylinder into an Erlenmeyer flask containing about 5 ml of 4N sulphuric acid.

Hydrogen peroxide analysis was done by titrating the 4 ml of product solution in sulphuric acid with 0.1 N (0.02M) KMnO_4 . The end point was light pink. The peroxide calculation was based on the following equation:

$$\text{Peroxide conc. (M)} = \left(\frac{5}{2}\right) (\text{KMnO}_4 \text{ vol. (ml)}) \left(\frac{\text{KMnO}_4 \text{ conc. (M)}}{\text{Sample volume}}\right) \quad (4.3)$$

CHAPTER 5

Reactor Modelling

5.1 Summary of reactions

For lucidity and ease of understanding the modelling work, the reactions occurring on the anode and cathode, discussed previously in Chapter 2, are summarized here.

Reactions on the cathode:

Reactions on the anode:

The overall reaction in alkaline solutions derived by subtracting 0.5 times reaction (2.11) from reaction (2.3) is:

or subsequently the OH^- ions may be speciated by Na^+ ions to give alkaline peroxide:

Reaction (2.5) is a thermochemical reaction. It has been neglected in the modelling work as its first-order rate constant is very small ($8 \text{ e-}6 \text{ s}^{-1}$ at 41°C (measured)). The kinetics of this reaction are sufficiently slow that they have little effect on the concentration of peroxide in the reactor, where the residence time is of the order of 1 minute (Figure 5.4). Also, reaction (2.9) is thermodynamically the least likely to occur on the cathode in the presence of excess oxygen and hence it has also not been included in the model. Previous experience at UBC had showed negligible H_2 under similar conditions.

Figure 5.1 Determination of rate constant for peroxide decomposition at different temperatures (41 , 60 and 80°C) and 2M NaOH

Experiments were done in order to determine the rate constant for peroxide decomposition in feed NaOH solutions at three different temperatures i.e. 41, 60 and 80 °C. A 500 ml flask was filled with 200 ml of 2M NaOH solution with additives (0.002%_w Makon NF-12 and 0.1%_w DTPA). Hydrogen peroxide (30%_w H₂O₂) was added to the NaOH solution to make it ca. 0.2-0.3 M in peroxide. The flask was then kept in a constant water temperature bath at ~ 41 °C with a thermometer dipped in the NaOH solution to monitor the solution temperature. 4ml samples of the solution were periodically withdrawn from the flask and the peroxide concentration determined by titrating the sample with KMnO₄ (cf. section 4.6). Similar peroxide decomposition experiments were also done at 60 and 80 °C.

The peroxide decomposition kinetics at different temperatures (41, 60 and 80 °C) are shown in Figure 5.1. The rate constants at the three temperatures, i.e. 41, 60 and 80 °C, are 8e-6, 6e-5 and 7e-4 sec⁻¹ respectively.

The rate constants determined in Figure 5.1 are plotted against the inverse of temperature to determine the activation energy for peroxide decomposition in Figure 5.2. The activation energy ($E_{\text{H}_2\text{O}_2}$) for peroxide decomposition was calculated to be 1.02 e5 J mol⁻¹. Erdey and Inczedy (1955) have measured the activation energy for peroxide decomposition in alkaline solutions to be 8.4 e4 J mol⁻¹, and Enestova et al. (1985) found it to be 9.2 e4 J mol⁻¹.

Figure 5.2 Determination of activation energy for peroxide decomposition

5.2 Assumptions in the model

The following assumptions were made in modelling the electrochemical reactors for alkaline peroxide generation:

- 1) Convection through the diaphragm in the model is accounted for by choosing a value for the eddy diffusivity (D_{ed})
- 2) The conductivity of the electrolyte in the perforations is assumed to be independent of oxygen flow (i.e. the perforations are fully filled with electrolyte)
- 3) Plug flow reactor model
 - Zero axial dispersion (along the length of reactor)
 - Infinite lateral dispersion (through the thickness of the graphite felt cathode)

The assumption of zero axial dispersion was based on the low dispersion values that were determined by tracer tests which are described in the next section.

5.2.1 Tracer tests for measuring axial dispersion

To measure the extent of axial dispersion in the perforated bipole electrochemical reactor, tracer tests were done on the medium-sized reactor with a gasketed graphite felt cathode sandwiched between the two electrode plates as shown in Figure 5.3. The graphite felt was compressed to 3.2 mm and water and O_2 were fed from the bottom of the reactor and withdrawn from the top. A small amount of tracer (0.5 ml of 0.5%_w NaCl solution) was injected at the inlet of the reactor using a syringe in pulse mode (very short time span < 1 sec), the conductivity change was monitored with time at the reactor exit using a conductivity probe and the data (conductivity vs time) recorded using a computer.

Figure 5.3 Tracer test on medium reactor

The conductivity versus time data was converted to a relative concentration versus time graph and these graphs are shown for varying flows of oxygen and water in Figures 5.2 to 5.4.

Figure 5.4 Relative tracer concentration versus time for water flow ($6.66e-4 \text{ kg s}^{-1}$) in the medium reactor

Figure 5.5 Relative tracer concentration versus time for water flow ($6.66 \times 10^{-4} \text{ kg s}^{-1}$) and oxygen flow ($4.3 \times 10^{-5} \text{ kg s}^{-1}$) in the medium reactor

Figure 5.6 Relative tracer concentration versus time for water flow ($6.66 \times 10^{-4} \text{ kg s}^{-1}$) and oxygen flow ($7.1 \times 10^{-5} \text{ kg s}^{-1}$) in the medium reactor

To analyze the results of the tracer tests, equations describing the flow pattern (closed-closed boundary condition) based on Figure 5.7 were used in the present work [Levenspiel, 1972].

Figure 5.7 Flow pattern for the peroxide reactor [Levenspiel, 1972]

The variance for the graphs in Figures 5.4 to 5.6 is given by the following equation [Levenspiel, 1972]:

$$\sigma^2/\tau^2 = 2 \left(\frac{D}{U_L l_e} \right) - 2 \left(\frac{D}{U_L l_e} \right)^2 \left(1 - \exp \left\{ - \left(U_L l_e \right) / D \right\} \right) \quad (5.3)$$

where σ is the standard deviation of the curves in Figures 5.4 to 5.6 and τ is the residence time in the reactor.

σ is calculated as the deviation on the time axis from the mean comprising 68% of the area under the curve or equivalently as the time width with 61% of the peak on the Gaussian curves (Figures 5.4 to 5.6).

The average residence time τ in the reactor may be calculated from the following equation:

$$\tau = \frac{\text{Reactor volume for water flow}}{\text{liquid flow rate}} = \frac{\varepsilon_b t_b w l_e h_l}{\left(\frac{\text{liq}}{\rho_L} \right)} \quad (5.4)$$

where ε_b is the porosity of the graphite felt (0.87), t_b is the graphite felt thickness (3.2e-3 m), w is the width of the reactor (0.04 m), l_e is the length of the reactor (0.63 m), liq is the liquid flow rate (6.66e-4 kg s⁻¹), g is the gas flow rate (4.3 e-5 – 7.1e-5 kg s⁻¹), ρ_L is the liquid density (1000 kg m⁻³) and h_l is the liquid hold up in the reactor given by (cf. equation C-28):

$$h_l = 1 - 0.907 \left(\frac{liq}{(t_b w)} \right)^{-0.362} \left(\frac{g}{(t_b w)} \right)^{0.301} \quad (5.5)$$

where liq and g are liquid and gas flow rates in kg s⁻¹.

Based on equations (5.3) to (5.5) the dispersion numbers ($D/U_L l_e$) for the three different flow configurations are given in Table 5.1. In the expression for dispersion number D is the dispersion coefficient and U_L is the superficial liquid velocity (5.2e-3 m s⁻¹) for the cases described in Figures 5.4 to 5.6.

The water and O₂ flow rates correspond to the electrolyte and O₂ flow rates typically used in the electrochemical reactor for alkaline peroxide generation in the present work.

The dispersion number calculated from Figure 5.4 using equation 5.3 is for liquid (only) flow, whereas that in Figures 5.5 and 5.6 are for liquid (water) and gas (oxygen) phase. The dispersion numbers reported in Table 5.1 are for liquid (water) flow and have been calculated by accounting for the liquid hold-up h_l in the reactor.

Table 5.1 Dispersion number values

Figure	Water flow rate (liq: kg s ⁻¹)	O ₂ flow rate (g: kg s ⁻¹)	Liquid hold up (h _l)	Standard deviation (σ: s)	Mean residence time (τ: s)	Dispersion number (D/U _L l _e)
5.4	6.66e-4	-	1	7	104	0.002
5.5	6.66e-4	4.3e-5	0.65	6	69	0.004
5.6	6.66e-4	7.1e-5	0.58	6	61	0.005

As the values of the dispersion numbers were between low (< 0.002) and intermediate (< 0.025) [Levenspiel, 1972], zero axial dispersion was a reasonable assumption.

5.3 Single-cell reactor model

Figure 5.8 Single-cell reactor model

As shown in Figure 5.8, O₂ and NaOH solution enter the cell from the bottom and the product peroxide in alkaline solution exits the reactor at the top. Peroxide in the form of perhydroxyl ion, HO₂⁻ is generated on the three-dimensional (3D) graphite felt cathode via reaction (2.3) by the reduction of oxygen and water.

Hydroxyl ions together with perhydroxyl formed on the cathode are transferred through the diaphragm by their convective, diffusive and migrative flux. These ions

undergo oxidation at the nickel mesh and Grafoil anode via reactions (2.10) and (2.11). The microporous polypropylene/polyethylene diaphragm provided between the cathode and the anode suppresses the loss of perhydroxyl ions (Chapter 2).

First a model was developed to determine the peroxide current efficiency and specific energy on a single-cell reactor (Figure 5.8). The modelling scheme entailed considering a differential cross section of the reactor (cf. Figure 5.8) and writing material, voltage and energy balances for this differential volume. The reactor was then integrated from the inlet (bottom) to the outlet (top) along the length of the reactor by forward differencing. The single-cell modelling work is discussed in detail in Appendix C and only the voltage balance is described here.

5.3.1 Voltage (a.k.a. charge) balance equations

Assuming the total superficial current density in the differential section (Figure 5.8) of the anode as i kA m^{-2} (not known a priori), the superficial current density on the anode due to perhydroxyl ion oxidation (2.10) is the sum of the diffusive, convective and migrative fluxes and is given by:

$$i_{\text{HO}_2^-} = \frac{(D_{\text{dHO}_2^-} + D_{\text{ed}})(C_{\text{HO}_2^-} - 0)F}{t_d} + \frac{0.001D_{\text{dHO}_2^-}F^2 C_{\text{HO}_2^-}i}{k_{\text{apd}}RT} \quad (5.6)$$

Convective flux may be accounted for by introducing an eddy diffusivity term D_{ed} in the diffusive component in equation (5.6).

The superficial current density due to hydroxyl ion oxidation (2.11) on the anode is given by:

$$i_{\text{OH}^-} = i - i_{\text{HO}_2^-} \quad (5.7)$$

Likewise the superficial current density on the anode due to diffusive, convective and migrative flux (Equation A-28) of hydroxyl ions is given by:

$$i_{OH^-} = \frac{(D_{dOH^-} + D_{ed})(C_{OH^-} - C_{aOH^-})F}{t_d} + 0.001D_{dOH^-}F^2i \left(\frac{C_{OH^-} + C_{aOH^-}}{2k_{apd}RT} \right) \quad (5.8)$$

where C_{aOH^-} is the concentration of hydroxyl ions at the anode. This hydroxyl concentration is not known a priori and may be calculated by rearranging equation (5.8) in terms of C_{aOH^-} .

To account for the migrative flux of hydroxyl ions in (5.8), the concentration is averaged across the diaphragm i.e. $(C_{OH^-} + C_{aOH^-})/2$.

Equation (5.8) is used to derive the equation for hydroxyl ion concentration (C_{aOH^-}) at the anode using the following equations:

$$\text{coef}_1 = \frac{(D_{dOH^-} + D_{ed})F}{t_d} \quad (5.9)$$

$$\text{coef}_2 = \frac{D_{dOH^-}F^2i}{2k_{apd}RT} \quad (5.10)$$

$$C_{aOH^-} = \frac{(i_{OH^-} - (\text{coef}_1 + \text{coef}_2)C_{OH^-})}{(\text{coef}_2 - \text{coef}_1)} \quad (5.11)$$

The equilibrium potential for reaction (2.3) on the cathode is given by:

$$V_{rc1} = -0.076 - \left(\frac{RT}{2F} \right) \ln \left(\frac{C_{HO2^-} C_{OH^-}}{P_{O_2}} \right) \quad (5.12)$$

and for reaction (2.4) is given by

$$V_{rc2} = 0.878 - \left(\frac{RT}{2F} \right) \ln \left(\frac{C_{OH^-}^3}{C_{HO2^-}} \right) \quad (5.13)$$

The major reaction occurring on the anode is the oxidation of hydroxyl ions (2.11). The perhydroxyl ions reaching the anode are assumed to be completely oxidized in the model.

The equilibrium potential for hydroxyl ion oxidation (2.11) is given by:

$$V_{ra} = 0.401 - \left(\frac{RT}{4F} \right) \ln \left(\frac{C_{aOH^-}^4}{P_{O_2}} \right) \quad (5.14)$$

The over-potential on the anode due to reaction (2.11) is given by:

$$\eta_a = a_a + b_a \log(i_{OH^-}) \quad (5.15)$$

where a_a and b_a are Tafel constants

The diaphragm potential drop assuming uniform electrolyte concentration in diaphragm is given by:

$$V_d = 1000 \frac{it_d}{k_{apd}} \quad (5.16)$$

Oxidation of perhydroxyl ions on the anode is not considered for the purpose of voltage balance.

The real current density based on the Butler-Volmer equation on the cathode for perhydroxyl ion formation (2.3) is given by:

$$j_{HO_2^-} = \frac{2F k^0_1 \exp \left[\left(\frac{-E_{a1}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_O C_{O_2} \exp \left[\left(\frac{-\alpha_1 F}{RT} \right) (\phi_s - \phi_b - V_{rc1}) \right]}{k_O + k^0_1 \exp \left[\left(\frac{-E_{a1}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_O C_{O_2} \exp \left[\left(\frac{-\alpha_1 F}{RT} \right) (\phi_s - \phi_b - V_{rc1}) \right]} \quad (5.17)$$

where k^0_1 is the rate constant for reaction (2.3) at 288 K and k_O and $k_{HO_2^-}$ are the mass transfer coefficients for oxygen and perhydroxyl ion through the electrolyte respectively.

Similarly for the perhydroxyl ion reduction reaction (2.4) the real current density is given by:

$$j_{OH^-} = \frac{2F k^0_2 \exp \left[\left(\frac{-E_{a2}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_{HO_2^-} C_{HO_2^-} \exp \left[\left(\frac{-\alpha_2 F}{RT} \right) (\phi_s - \phi_b - V_{rc2}) \right]}{k_{HO_2^-} + k^0_2 \exp \left[\left(\frac{-E_{a2}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_{HO_2^-} C_{HO_2^-} \exp \left[\left(\frac{-\alpha_2 F}{RT} \right) (\phi_s - \phi_b - V_{rc2}) \right]} \quad (5.18)$$

where k_2^0 is the rate constant for reaction (2.4) at 288 K and ϕ_s and ϕ_b are the electrode and electrolyte potential respectively at any point in the graphite felt cathode (Figure 5.9).

Equation (5.17) and (5.18) are derived from the fact that at the electrode boundary the rate of mass transfer is equal to the rate of reaction i.e.

$$k_m (C_{Rb} - C_{Rs}) = k^0 C_{Rs} \exp \left[\left(-\frac{E_a}{R} \right) \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \exp \left[\left(-\frac{\alpha F}{RT} \right) (\phi_s - \phi_b - V_{rc}) \right] \quad (5.19)$$

where C_{Rb} and C_{Rs} are the concentrations of the reduced species in the bulk electrolyte and at the electrode surface respectively.

Rewriting equation (5.19) for C_{Rs} and replacing T^* by 288 K and E_a , k^0 , α , V_{rc} , k_m and C_{Rb} by E_{a1} , k_1^0 , α_1 , V_{rc1} , k_O and C_{O2} , equation (5.17) is arrived at, and by E_{a2} , k_2^0 , α_2 , V_{rc2} , k_{HO2} and C_{HO2} , equation (5.18) is derived.

The voltage balance equations on the graphite felt 3D cathode (Figure 5.9) are a complex function of electrode, electrolyte potential and current densities for perhydroxyl ion formation (2.3) and reduction (2.4) and are given by the second-order non-linear differential equation:

$$\nabla^2 (\phi_s - \phi_b) = -s \left(\frac{1}{k_{aps}} + \frac{1}{k_{apb}} \right) j \quad (5.20)$$

Equation (5.20) may be derived by differentiating the equation for Ohm's law in the electrode (5.21) and electrolyte phase (5.22) and taking the divergence of the current transferred from the electrode to electrolyte phase (5.23):

$$\nabla \phi_s = -\frac{i_s}{k_{aps}} \quad (5.21)$$

$$\nabla \phi_b = -\frac{i_b}{k_{apb}} \quad (5.22)$$

$$\nabla \cdot i_s = -\nabla \cdot i_b = s j_{\text{cathode}} \quad (5.23)$$

where i_s and i_b are the current densities in electrode and electrolyte phase respectively.

Equivalently, for one dimension (5.20) reduces to:

$$\frac{d^2(\phi_s - \phi_b)}{dx^2} = s \left(\frac{1}{k_{aps}} + \frac{1}{k_{apb}} \right) j \quad (5.24)$$

where $j_{\text{cathode}} = f(\phi_s, \phi_b)$ is given by:

$$j_{\text{cathode}} = j_{\text{HO}_2^-} + j_{\text{OH}^-} \quad (5.25)$$

Equation (5.24) is equivalent to solving the following four first-ordered D.E.s:

$$Zb = \frac{d\phi_b}{dx} \quad (5.26)$$

$$\text{boundary condition: } \phi_b = V_{cf} \quad \text{at } x = 0 \quad (5.27)$$

$$Zs = \frac{d\phi_s}{dx} \quad (5.28)$$

$$\text{boundary condition: } \phi_s = 0 \quad \text{at } x = t_b \quad (5.29)$$

$$\frac{dZb}{dx} = \frac{-sj}{k_{apb}} \quad (5.30)$$

$$\text{boundary condition: } d\phi_b/dx = -i/k_{apb} \quad \text{at } x = 0 \quad (5.31)$$

$$\frac{dZs}{dx} = \frac{sj}{k_{aps}} \quad (5.32)$$

$$\text{boundary condition: } d\phi_s/dx = 0 \quad \text{at } x = 0 \quad (5.33)$$

Equations (5.20) to (5.33) cannot be solved easily as the current density (i) on the anode is not known, a priori. Thus the superficial current density (i) is guessed and the voltage balance iterated to arrive at the solution of the differential equation (5.20). The solution methodology is discussed in the voltage balance algorithm (Figure 5.10).

Figure 5.10 provides a flowsheet for the voltage balance, i.e. to solve Poisson's equation in the 3D cathode given by (5.24). Poisson's equation is a second-order nonlinear differential equation (5.24) and is solved by converting it into four first-order equations given by (5.26), (5.28), (5.30) & (5.32). These four first-order equations have their respective boundary conditions in equation (5.27), (5.29), (5.31) & (5.33). The boundary condition (5.29) is known at $x = t_b$ and not at $x = 0$ so the value of the boundary

condition (5.29) at $x = 0$ has to be guessed to solve the differential equations. The four first order differential equations (5.26), (5.28), (5.30) & (5.32) are solved using a 5th order Runge-Kutta shooting method that aims for the boundary condition for the cathode matrix potential, ϕ_s at $x = t_b$. If this potential ϕ_s is found to be zero then the total current transferred from the electrolyte to the cathode matrix is calculated. If this transferred current matches the initial guessed current (i) on the anode then the voltage balance is converged, otherwise these steps are repeated till the problem is solved.

The single-cell model developed for the peroxide reactor does not converge for two-cells especially with multiple reactions occurring on the cathode. Therefore another model was developed for the two-cell reactor with a perforated bipole. This alternate two-cell model is discussed in the next section.

ϕ_s, ϕ_b	= electrode, electrolyte potential	V
η_a	= anode overpotential	V
V_{cf}	= cathode face potential	V
V_d	= diaphragm IR drop	V
V_r	= reactor voltage	V
V_{ra}	= equilibrium voltage for reaction (2.10) on the anode	V
k_{apb}	= effective electrolyte conductivity	$S m^{-1}$
k_{aps}	= effective matrix (felt) conductivity	$S m^{-1}$
$j_{cathode}$	= real current density on the 3D cathode due to reaction (2.3) & (2.4)	$kA m^{-2}$
s	= specific surface area of 3D cathode	m^{-1}
l_e	= length of the reactor	m
t_b	= thickness of cathode bed (graphite felt)	m
Δz	= thickness of the cross-section in Figure 5.8	m
w	= width of the reactor	m

Figure 5.9 Voltage balance for one length increment on a single-cell reactor

Figure 5.10 Flow chart for voltage balance for one length increment on a single-cell reactor

5.4 Two-cell bipolar reactor model

Figure 5.11 Two-cell reactor model

Figure 5.11 shows the two-cell reactor assembly that was employed to carry out the experimental work on the multi-cell system. The two-cell assembly is similar to the single-cell assembly of Figure 5.8 but with a difference that here two cells are adjacent to one another in series. The central perforated Grafoil sheet is a bipolar electrode. It behaves as an anode on one side and a cathode on the other. This perforated bipolar electrode allows the passage of current due to electrolyte in the perforations that provide an electrical path between the two sides of the bipolar electrode. This current that bypasses the cell through the perforations, as may be seen from Figure 5.12, does so without undergoing any electrochemical reactions at the electrode. Therefore this current is a source of loss in current efficiency. This loss in current efficiency may be calculated based on the illustration in Figure 5.13.

Figure 5.12 Current bypass through a perforation assumes perforations filled fully with electrolyte (NaOH)

Figure 5.13 Current bypass mechanism in a two-cell assembly

The perforations normally have flows of gas and liquid in them; however, knowing the exact amounts of gas and liquid in each perforation is difficult to determine. Also, fully-filled perforations with electrolyte provide a sufficient guide for scaling-up the electrochemical reactor. Therefore, the perforations in the bipole electrochemical reactor are assumed to be completely filled with electrolyte (NaOH).

It may be observed from Figure 5.13 that current $I_1 + I_2$ flows from the right through the diaphragm into the electrolyte phase. Of this total current ($I_1 + I_2$), current I_1 flows into the cathode or electrode phase. Current I_2 bypasses the electrode through the perforation. So the useful current for cell 1 is only I_1 . However, for cell 2, all of the current ($I_1 + I_2$) passes into the electrode phase before exiting the reactor. So current I_1 passes through the cathode beds of both the cells and does electrochemical reactions on the cathode bed. Whereas current I_2 is transferred via electrochemical reactions (2.3), (2.4) and (2.9) in the cathode bed of cell 2 only. For this reason the current bypass may be derived from the following equation:

$$\text{Fractional current bypass for two cells in series} = \frac{I_2}{2(I_1 + I_2)} \quad (5.34)$$

Likewise,

$$\text{Fractional current bypass for three cells in series} = \frac{2I_2}{3(I_1 + I_2)} \quad (5.35)$$

and

$$\text{Fractional current bypass for } n_{\text{cell}} \text{ cells in series} = \frac{(n_{\text{cell}} - 1)I_2}{(n_{\text{cell}})(I_1 + I_2)} \quad (5.36)$$

If n_{cell} is large (> 20) then

$$\text{Fractional current bypass} = \frac{I_2}{(I_1 + I_2)} \quad (5.37)$$

To calculate the currents I_1 and I_2 , a voltage balance on the two-cell reactor is required. That is, Poisson's equation (5.24) has to be solved twice in each of the cathode beds. The boundary condition of ϕ_s at the bipolar electrode (8) in Figure 5.10 is not known and needs to be guessed a priori, shooting for the boundary condition of $\phi_s = 0$ at

the feeder cathode of cell 2. Simultaneously the sum of the current transferred due to the electrochemical reactions (2.3) and (2.4) at the cathode in cell 1 and the bypass current through the perforations must also match the current transferred at the cathode in cell 2 due the same electrochemical reactions (2.3) and (2.4). However a numerical solution along the lines of the single-cell reactor as discussed previously leads to even more complications in terms of convergence if applied to the two-cell reactor system. This strategy was therefore discarded and another method of finding the solution sought.

Figure 5.14 Voltage balance on a two-cell reactor

The bipolar reactor section shown in Figure 5.14 is modelled based on a voltage balance. The methodology involves breaking the total voltage balance into a combination of series and parallel resistances as shown in Figure 5.15. The 3D cathode is broken up into series and parallel circuits based on the effective electrode and electrolyte

conductivity given by k_{aps} and k_{apb} respectively. At the anode of cell 1 the superficial current density (based on the cross-sectional area of the cut section in Figure 5.11) is $j(1)$. The 3D cathode bed is broken up into $(n-1)/4$ sections. Here $n = 4m + 1$ (m is an integer) is the number of current densities $j(1), j(2), \dots, j(n)$. The even current densities $j(2), j(4), \dots, j(n-1)$ in the 3D cathode are due to reaction (2.3) and the odd current densities $j(3), j(5), \dots, j(n)$ are due to reaction (2.4). By forming n independent equations one can solve for the n current densities $j(1), j(2), \dots, j(n)$. The n equations can be obtained by formulating the series and parallel resistances of Figure 5.15 into n independent circuits. These independent circuits are solved using Kirchoff's law of currents. The n equations can then be solved for the unknown current densities $j(1), j(2), \dots, j(n)$ using Newton's method for the solution of nonlinear equations.

The two-cell reactor model can be used for a single-cell by setting the perforation coverage = 0.001 so as to make the current bypass insignificant in comparison to the Faradaic current.

$j(1)$	: Superficial current density	$A\ m^{-2}$
$j(2), j(4), \dots, j(n-1)$	: Current densities for peroxide generation reaction (1) where $n = 4m + 1$, m is an integer	$A\ m^{-2}$
$j(3), j(5), \dots, j(n)$	: Current densities for peroxide reduction reaction (2)	$A\ m^{-2}$
k_{apb}	: Effective electrolyte conductivity in cathode bed	$S\ m^{-1}$
k_{apd}	: Effective diaphragm conductivity	$S\ m^{-1}$
k_{perf}	: Effective electrolyte conductivity in perforation	$S\ m^{-1}$
k_{aps}	: Effective electrode conductivity of cathode bed	$S\ m^{-1}$
V_{ra}	: Equilibrium potential for hydroxyl oxidation at anode	V
V_{rc1}	: Equilibrium potential for perhydroxyl generation at cathode	V
V_{rc2}	: Equilibrium potential for perhydroxyl reduction at cathode	V
$V_{contact1}$	: Contact voltage drop between grafoil and graphite on cell 1	V
$V_{contact2}$	: Contact voltage drop between grafoil and graphite on cell 2	V
$V_{grafoil}$	: Voltage drop on grafoil	V
η_{aOH-}	: Over potential for hydroxyl oxidation at anode	V
η_{c1}	: Over potential for perhydroxyl generation (2.3) at cathode	V
η_{c2}	: Over potential for perhydroxyl reduction (2.4) at cathode	V

Figure 5.15 Electronic analogue of voltage balance for one length increment on a two-cell reactor

5.4.1 Parameters in the model

The parameters used in modelling the two-cell reactor for peroxide generation are defined in Table 5.2:

Table 5.2 Parameters in the model

Parameter	Meaning	Source	Value	Units
c_l	Electrolyte heat capacity	[Hooker, 1977] Averaged (298-353 K)	4	$\text{kJ kg}^{-1}\text{K}^{-1}$
c_g	Gas (O_2) heat capacity	[CRC handbook, 1986] Averaged (298-353 K)	0.9	$\text{kJ kg}^{-1}\text{K}^{-1}$
$C_{\text{HO}_2^-}$	perhydroxyl ion concentration	measured	$1\text{e-}6$ (reactor inlet)*	kmol m^{-3}
C_{OH^-}	hydroxyl concentration	measured	1-2 (reactor inlet)	kmol m^{-3}
C_{Na^+}	sodium ion concentration	measured	1-2	kmol m^{-3}
D_{ed}	eddy diffusivity through the diaphragm	to fit the experimental curve	0- $2\text{e-}8$	$\text{m}^2 \text{s}^{-1}$
$D_{\text{HO}_2^-}^0$	diffusivity of perhydroxyl ion at infinite dilution	[CRC handbook, 1986] at 298 K	$1.5\text{e-}9$	$\text{m}^2 \text{s}^{-1}$

$D^0_{OH^-}$	diffusivity of hydroxyl ion at infinite dilution	[CRC handbook, 1986] at 298 K	5.3e-9	$m^2 s^{-1}$
$D^0_{Na^+}$	diffusivity of sodium at infinite dilution	[CRC handbook, 1986] at 298 K	1.3e-9	$m^2 s^{-1}$
$D^0_{O_2}$	Diffusivity of oxygen at infinite dilution	[CRC handbook, 1986] at 298 K	2.4e-9	$m^2 s^{-1}$
g	gas flow rate per cell	small cell (measured)	1.24e-5	$kg s^{-1}$
		medium cell (measured)	1.7e-5	
liq	liquid flow rate per cell	small cell (measured)	3.4e-4	$kg s^{-1}$
		medium cell (measured)	6.7e-4	
d_f	graphite felt fibre diameter	Metaullics systems Inc.	2e-5	m
ϵ_b	graphite felt porosity after compression	small reactor [Oloman, 1991]	0.9	dimensionless
		medium reactor [Oloman, 1991]	0.87	
ϵ_d	diaphragm porosity	SCIMAT 700/20	0.80	dimensionless
		SOLUPOR E075-9H06A.	0.76	

ε_0	graphite porosity felt before compression	Metaullics systems Inc.	0.95	dimensionless
k_1^0	rate constant for reaction (2.3)	[Sudoh et al, 1985a] at 288 K	5e-7	m s^{-1}
k_2^0	rate constant for reaction (2.4)	[Sudoh et al, 1985a] at 288 K	1.6e-9	m s^{-1}
α_1	charge transfer coefficient for single step of reaction (2.3)	[Sudoh et al, 1985a] at 288 K	0.543	dimensionless
α_2	charge transfer coefficient for single step of reaction (2.4)	[Sudoh et al, 1985a] at 288 K	0.263	dimensionless
E_{a1}	activation energy for reaction (2.3) on carbon	[Kinoshita, 1992]	25530	J mol^{-1}
E_{a2}	activation energy for reaction (2.4) on carbon	[Kinoshita, 1992]	25530	J mol^{-1}
t_b	thickness of graphite felt (compressed)	measured	3.2 e-3	m
t_d	thickness of diaphragm	SCIMAT 700/20	120 e-6	m
		SOLUPOR E075-9H06A.	39 e-6	

t₀	thickness of graphite felt (un - compressed)	small reactor (as received)	6.4e-3	m
		medium reactor (as received)	8.2e-3	
l_e	length of the reactor	small reactor	0.12	m
		medium reactor	0.63	
w	width of the reactor	small reactor	0.025	m
		medium reactor	0.04	
T	reactor temperature	measured	293 (reactor inlet)	K
P	reactor pressure	measured	900 (reactor inlet)	kPa (abs.)
V_r	reactor voltage	measured	1.5-6.5	V
j_{0a}	Exchange current density for reaction (2.11) on nickel anode	[Kinoshita, 1992] at 296 K assumed constant for entire reactor	1.1 e-7	A m ⁻²
b_a	Tafel slope for reaction (2.11) on the anode	[Kinoshita, 1992] at 296 K assumed constant for entire reactor	0.043	V decade ⁻¹
k_{contact}	area conductivity between Grafoil and graphite felt	measured	5000	S m ⁻²
k_{grafoil}	conductivity of Grafoil	measured	1e4	S m ⁻¹
n	circuits solved (Figure 5.15)	small and medium cell	77	dimensionless

ln	number of length increments in Figure 5.11	small cell	20	dimensionless
		medium cell	100	

** The inlet concentration of perhydroxyl ions is kept as $1\text{e-}6 \text{ kmol m}^{-3}$ to avoid convergence close-up problems in modelling

- I_{reactor} is the total current fed to the reactor, *Amperes* (initially set to zero)

5.4.2 Voltage, material and energy balances

Before discussing the modelling algorithm it is essential to define all the equations that have been used in the modelling work. Based on their nature, the equations could be clustered into separate groups.

Vapour pressure of water and the reactor pressure

The vapour pressure of NaOH solution $< 10\%_w$ [Hooker, 1977] is not substantially different from pure water and, therefore, may be approximated from the Antoine's equation for pure water [Reklaitis, 1983] using:

$$P_{\text{H}_2\text{O}} = e^{\left(16.5362 - \frac{3985.44}{T - 38.9974}\right)} \quad \text{kPa} \quad (5.38)$$

where T is the temperature in K.

The O_2 pressure may be calculated by subtracting the vapour pressure of water from the reactor pressure:

$$P_{\text{O}_2} = P - P_{\text{H}_2\text{O}} \quad \text{kPa(abs.)} \quad (5.39)$$

Liquid and gas densities

Liquid density (kg m^{-3}) for the electrolyte (NaOH) is calculated by least squares fitting the data for NaOH density versus concentration [CRC handbook, 1986]:

$$\rho_L = 1000 (1 + 0.04C_{\text{Na}^+}) \quad \text{kg m}^{-3} \quad (5.40)$$

Gas density is estimated using the ideal gas law (ignoring the water vapour):

$$\rho_G = \frac{M_{O_2} P_{O_2}}{RT} \quad kg\ m^{-3} \quad (5.41)$$

Liquid and gas viscosities

Liquid viscosity is calculated by least squares fitting the data for NaOH viscosity versus temperature and concentration [CRC handbook, 1986]:

$$\mu_L = 0.001(1 + 0.5 C_{Na+}) 10^{-10.73 + 1828/T + 0.01966T - 1.466e-5 T^2} \quad kg\ m^{-1}\ sec^{-1} \quad (5.42)$$

where C_{Na+} is the concentration of sodium ion (M) and T is the temperature (K).

Gas (O_2) viscosity is calculated by least square fitting the data for O_2 viscosity versus temperature [CRC handbook, 1986]:

$$\mu_G = 1e-6[18.11 + 0.6632 T - (1.879e-4)T^2] \quad kg\ m^{-1}\ sec^{-1} \quad (5.43)$$

where T is the temperature in K.

Diffusivities of various species

The diffusivities of HO_2^- , OH^- , Na^+ and O_2 in NaOH are calculated using the Stokes-Einstein equation ($D\mu/T = \text{constant}$) [Oloman, 1996]:

$$D_{HO_2^-} = \frac{0.001D_{HO_2^-}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (5.44)$$

$$D_{OH^-} = \frac{0.001D_{OH^-}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (5.45)$$

$$D_{Na^+} = \frac{0.001D_{Na^+}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (5.46)$$

$$D_{O_2} = \frac{0.001D_{O_2}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (5.47)$$

The effective diffusivities of HO_2^- and OH^- ions in the diaphragm are affected by the porosity of diaphragm and according to Neale and Nader (1973) are given by:

$$D_{dHO_2} = \frac{2D_{HO_2} \cdot \varepsilon_d}{3 - \varepsilon_d} \quad m^2 s^{-1} \quad (5.48)$$

$$D_{dOH} = \frac{2D_{OH} \cdot \varepsilon_d}{3 - \varepsilon_d} \quad m^2 s^{-1} \quad (5.49)$$

Henry's constant

For mildly soluble gases, the gas (O_2) to liquid (NaOH) equilibrium is defined using Henry's law [Treybal, 1993]:

$$C_{O_2} = \frac{(P_{O_2}/101)}{H} \quad kmol m^{-3} \quad (5.50)$$

where H is the Henry's constant for oxygen dissolution in NaOH (Appendix B) and is given by:

$$H = \frac{H_O}{(C_{NaOH, O_2}/C_{H_2O, O_2})} \quad kmol kg^{-1} m^{-2} sec^2 \quad (5.51)$$

and H_O is the Henry's constant for O_2 dissolution in H_2O (Appendix B) and is given by:

$$H_O = e^{\left[\frac{0.046T^2 + 203.35T \ln\left(\frac{T}{298}\right) - (299.378 + 0.092T)(T-298)20.591e3}{8.3144T} \right]} \quad kmol kg^{-1} m^{-2} sec^2 \quad (5.52)$$

where T is the temperature in K.

The ratio $C_{NaOH, O_2}/C_{H_2O, O_2}$ is calculated using the Sechenov equation (Appendix B).

Specific surface area of the graphite felt cathode

Specific surface is the area per unit volume of the graphite felt and it is given by:

$$s = 4 \frac{(1 - \varepsilon_b)}{d_f} \quad m^{-1} \quad (5.53)$$

Fluid dynamics and mass transfer in the reactor

The two-phase pressure gradient based on Hodgson and Oloman's (1999) correlation is given by:

$$\nabla P_{LG} = \frac{\Delta P_{LG}}{\Delta z} = \left(\frac{\text{liq}}{t_b w} \right) \left(0.36 + 1.182 \left(\frac{g}{\text{liq}} \right)^{0.618} \right)^2 \quad kg \, m^{-2} \, sec^{-2} \quad (5.54)$$

The liquid hold up is given by [Hodgson and Oloman, 1999]:

$$h_l = 1 - 0.907 \left(\frac{\text{liq}}{t_b w} \right)^{-0.362} \left(\frac{g}{t_b w} \right)^{0.301} \quad (5.55)$$

The overall mass transfer capacity coefficient for oxygen is given by [Hodgson and Oloman, 1999]:

$$k_o = 5.9 \left(\frac{\text{liq}}{t_b w} \right)^{0.372} \left(\frac{g}{t_b w} \right)^{0.301} \left(\frac{1}{s} \right) \quad m \, s^{-1} \quad (5.56)$$

where liq and g are mass flow rates of liquid and gas through the cathode bed per cell.

Assuming a constant film thickness, the mass transfer coefficient for perhydroxyl ions may be approximated by:

$$k_{HO_2^-} = \frac{k_o D_{HO_2^-}}{D_{O_2}} \quad m \, s^{-1} \quad (5.57)$$

Effective electrode and electrolyte conductivities

The electrolyte conductivity is approximated by fitting a polynomial equation to NaOH conductivity versus NaOH concentration data [CRC handbook, 1986] using a temperature coefficient for conductivity increase of 0.023 per degree K rise in temperature [Oloman, 1996]:

$$k_{apl} = (0.0726 + 19.576 C_{Na^+} - 3.035 C_{Na^+}^2) (1 + 0.023 (T - 293)) \quad S \, m^{-1} \quad (5.58)$$

The effective electrolyte conductivities in the diaphragm (k_{apd}) and the graphite felt cathode (k_{apb}) are calculated from the work of Neale and Nader (1973):

$$k_{apd} = \frac{2 k_{apl} \varepsilon_d}{(3 - \varepsilon_d)} \quad S m^{-1} \quad (5.59)$$

$$k_{apb} = \frac{2 k_{apl} \varepsilon_b h_1}{(3 - \varepsilon_b h_1)} \quad S m^{-1} \quad (5.60)$$

The effective electrode conductivity of the cathode matrix is calculated from the correlation of Oloman et al. (1991):

$$k_{aps} = 10 + 2800 \left(\frac{1 - \varepsilon_b}{\varepsilon_o} \right)^{1.55} \quad S m^{-1} \quad (5.61)$$

The perforations are assumed to be fully filled with electrolyte at all times in the model and the conductivity of the perforations is given by:

$$k_{perf} = k_{apl} \quad S m^{-1} \quad (5.62)$$

Current densities and potentials on the cathode and anode

The current density for reaction (2.3) cannot be increased beyond a certain value due to mass transfer constraints and this limiting value is known as the mass transfer limited current density for O_2 transfer to the graphite felt and is given by:

$$j_{lim1} = 2000 F k_o C_{O_2} \quad A m^{-2} \quad (5.63)$$

and the mass transfer limited current density for perhydroxyl ions to the graphite felt surface is given by:

$$j_{lim2} = 2000 F k_{HO_2^-} C_{HO_2^-} \quad A m^{-2} \quad (5.64)$$

The total superficial current density on the anode (Figure 5.15) is denoted by $j(1)$ $A m^{-2}$. The current densities on the cathode due to perhydroxyl ion formation (2.3) are

denoted as $j(2), j(4), \dots, j(n-1)$ and due to perhydroxyl ion reduction (2.4) is denoted as $j(3), j(5), \dots, j(n)$. Note here $n = 4m + 1$ where m is a positive integer.

The equilibrium potential for reaction (2.3) on the cathode is given by:

$$V_{rc1} = -0.076 - \left(\frac{RT}{2F} \right) \ln \left(\frac{C_{HO2^-} \cdot C_{OH^-}}{P_{O_2}} \right) \quad V \quad (5.65)$$

and for reaction (2.4) is given by:

$$V_{rc2} = 0.878 - \left(\frac{RT}{2F} \right) \ln \left(\frac{C_{OH^-}^3}{C_{HO2^-}} \right) \quad V \quad (5.66)$$

The major reaction occurring on the anode is the oxidation of hydroxyl ions (2.11). The perhydroxyl ions reaching the anode are assumed to be completely oxidized in the model.

The equilibrium potential for hydroxyl ion oxidation (2.11) is given by:

$$V_{ra} = 0.401 - \left(\frac{RT}{4F} \right) \ln \left(\frac{C_{aOH^-}^4}{P_{O_2}} \right) \quad V \quad (5.67)$$

When carrying out voltage, material and energy balances over the first differential section shown in Figure 5.11, C_{aOH^-} is assumed to be equal to C_{OH^-} .

The over-potential on the anode due to reaction (2.11) is given by:

$$\eta_a = a_a + b_a \ln(j(1)) \quad V \quad (5.68)$$

where a_a and b_a are Tafel constants for reaction (2.11) on nickel and are given by:

$$a_a = \frac{-RT \ln(j_{0a})}{\alpha_a F} \quad V \quad (5.69)$$

$$b_a = \frac{RT}{\alpha_a F} \quad V \text{ decade}^{-1} \quad (5.70)$$

The oxidation of perhydroxyl ions on the anode is not considered in the voltage balance; however the perhydroxyl loss through the diaphragm is accounted for.

The diaphragm potential drop is given by:

$$V_d = \frac{j(l)t_d}{k_{apd}} \quad V \quad (5.71)$$

The over-potential due to perhydroxyl ion formation (2.3) is given by:

$$\eta_{cl} = a_{cl} + b_{cl} \ln(j(k)) \quad V \quad (5.72)$$

where $k = 2, 4, \dots, (n-1)$. a_{cl} and b_{cl} are Tafel parameters for reaction (2.3) and are given by:

$$a_{cl} = \frac{-RT \ln(j_{01})}{\alpha_1 F} \quad V \quad (5.73)$$

$$b_{cl} = \frac{RT}{\alpha_1 F} \quad V \text{ decade}^{-1} \quad (5.74)$$

where j_{01} is the exchange current density for reaction (2.3) on graphite and is given by:

$$j_{01} = 2000 F k^0 \exp \left[\left(\frac{-E_{a1}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] C_{O_2} \exp \left(\frac{-\alpha_1 F V_{rel}}{RT} \right) \quad A \text{ m}^{-2} \quad (5.75)$$

The over-potential due to perhydroxyl ion reduction (2.4) is given by:

$$\eta_{c2} = a_{c2} + b_{c2} \ln(j(k)) \quad V \quad (5.76)$$

where $k = 3, 5, \dots, n$. a_{c2} & b_{c2} are Tafel parameters for reaction (2.4) and are given by:

$$a_{c2} = \frac{-RT \ln(j_{02})}{\alpha_2 F} \quad V \quad (5.77)$$

$$b_{c2} = \frac{RT}{\alpha_2 F} \quad V \text{ decade}^{-1} \quad (5.78)$$

where j_{02} is the exchange current density for reaction (2.3) on graphite and is given by:

$$j_{02} = 2000 F k^0 \exp \left[\left(\frac{-E_{a2}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] C_{HO_2} \exp \left(\frac{-\alpha_2 F V_{rel}}{RT} \right) \quad A \text{ m}^{-2} \quad (5.79)$$

Using these equations and Kirchoff's laws for currents (see Appendix D) the circuit in Figure 5.15 is solved for currents $j(1)$ to $j(n)$ for the differential section shown in Figure 5.11.

The superficial current density on the anode due to perhydroxyl ion oxidation (2.10) is the sum of diffusive, convective and migrative flux and is given by:

$$i_{1\text{HO}_2^-} = \frac{(D_{\text{dHO}_2^-} + D_{\text{ed}})(C_{1\text{HO}_2^-} - 0)F}{t_d} + \frac{j(1)D_{\text{dHO}_2^-}F^2 C_{1\text{HO}_2^-}}{k_{\text{apd}}RT} \quad \text{kA m}^{-2} \quad (5.80)$$

$$i_{2\text{HO}_2^-} = \frac{(D_{\text{dHO}_2^-} + D_{\text{ed}})(C_{2\text{HO}_2^-} - 0)F}{t_d} + \frac{j(1)D_{\text{dHO}_2^-}F^2 C_{2\text{HO}_2^-}}{k_{\text{apd}}RT} \quad \text{kA m}^{-2} \quad (5.81)$$

Convective flux may be accounted for by introducing an eddy diffusivity term D_{ed} in the diffusive component in equations (5.80) and (5.81).

The superficial current densities due to hydroxyl ion oxidation (2.11) on the anode of cell 1 and 2 are given by:

$$i_{1\text{OH}^-} = 0.001 j(1) - i_{1\text{HO}_2^-} \quad \text{kA m}^{-2} \quad (5.82)$$

$$i_{2\text{OH}^-} = 0.001 j(1) - i_{2\text{HO}_2^-} \quad \text{kA m}^{-2} \quad (5.83)$$

Likewise the superficial current density on the anode due to diffusive, convective and migrative flux of hydroxyl ions may be determined from the following equation:

$$i_{1\text{OH}^-} = \frac{(D_{\text{dOH}^-} + D_{\text{ed}})(C_{\text{OH}^-} - C_{\text{aOH}^-})F}{t_d} + \frac{0.001D_{\text{dOH}^-}F^2((C_{\text{OH}^-} + C_{\text{aOH}^-}))j(1)}{2k_{\text{apd}}RT} \quad \text{kA m}^{-2} \quad (5.84)$$

Here C_{aOH^-} is the concentration of hydroxyl ions at the anode. This concentration was assumed to be equal to C_{OH^-} for the first differential section in Figure 5.11. The subsequent values may be calculated by rearranging equation (5.84) in terms of C_{aOH^-} . In the migrative flux term of the hydroxyl ions, the concentration is averaged across the diaphragm, i.e. $(C_{\text{OH}^-} + C_{\text{aOH}^-})/2$.

Equation (5.84) can be rewritten to derive the equation for hydroxyl ion concentration (C_{aOH^-}) at the anode:

$$C_{aOH^-} = \frac{(i_{1OH^-} - (coef_1 + coef_2)C_{OH^-})}{(coef_2 - coef_1)} \quad kmol\ m^{-3} \quad (5.85)$$

where:

$$coef_1 = \frac{(D_{dOH^-} + D_{ed})F}{t_d} \quad (5.86)$$

$$coef_2 = \frac{D_{dOH^-} F^2 j(1)}{2k_{apd} RT} \quad (5.87)$$

Since the hydroxyl concentration does not differ much for cells 1 and 2, therefore the C_{aOH^-} term is calculated from equation (5.87) for both the cells.

The total currents flowing through the cathode bed of cells 1 and 2 for reaction (2.3) are given by equations (5.88) and (5.89), respectively, and for reaction (2.4) by (5.90) and (5.91), respectively:

$$\Sigma j_{1HO_2^-} = 0.001[j(2) + j(4) + \dots j((n-1)/2)] \quad kA\ m^{-2} \quad (5.88)$$

$$\Sigma j_{2HO_2^-} = 0.001[j((n-1)/2 + 2) + j((n-1)/2 + 4) + \dots j(n-1)] \quad kA\ m^{-2} \quad (5.89)$$

$$\Sigma j_{1OH^-} = 0.001[j(3) + j(5) + \dots j((n-1)/2 + 1)] \quad kA\ m^{-2} \quad (5.90)$$

$$\Sigma j_{2OH^-} = 0.001[j((n-1)/2 + 3) + j((n-1)/2 + 5) + \dots j(n)] \quad kA\ m^{-2} \quad (5.91)$$

Voltage balance equations

There are n currents to be calculated in the circuit in Figure 5.15 and these can be determined by solving n independent equations. The n independent equations can be obtained by applying Kirchoff's laws for current (cf. Appendix D).

Of the n equations, $(n-1)/4 - 1$ equations can be obtained by applying Kirchoff's law to the closed loop formed by the currents transferred from the electrolyte to the

cathode phase due to reaction (2.3) in two adjacent circuits in cell 1. This procedure yields:

$$b_{c1} \ln(j(2(k+1))) - b_{c1} \ln(j(2k)) + b_{c1} \ln(j_{lim1} - j(2k)) - b_{c1} \ln(j_{lim1} - j(2(k+1))) + j(1) \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{1}{k_{apb}} \right) - s \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{1}{k_{aps}} + \frac{1}{k_{apb}} \right) j_{sig1}(k) = 0 \quad (5.92)$$

where k varies from 1 to $(n-1)/4-1$ and

$$j_{sig1}(k) = j(2) + j(3) + \dots + j(2k) + j(2k+1) \quad A \, m^{-2} \quad (5.93)$$

Similarly another $(n-1)/4 - 1$ equations can be obtained by applying Kirchoff's law to the current transferred from the electrolyte to the cathode phase due to reactions (2.3) in the two adjacent circuits in cell 2. In this case:

$$b_{c1} \ln(j(2(k+2))) - b_{c1} \ln(j(2(k+1))) - s \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{1}{k_{aps}} + \frac{1}{k_{apb}} \right) j_{total}(k) + b_{c1} \ln(j_{lim1} - j(2(k+1))) - b_{c1} \ln(j_{lim1} - j(2(k+1))) + j(1) \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{1}{k_{apb}} \right) = 0 \quad (5.94)$$

where k varies from $(n-1)/4$ to $(n-1)/2 - 2$ and

$$j_{total}(k) = j((n-1)/2 + 2) + j((n-1)/2 + 3) + \dots + j(2k+2) + j(2k+3) \quad A \, m^{-2} \quad (5.95)$$

Another $(n-1)/2$ equations can be obtained by applying Kirchoff's law to the closed loop formed by currents transferred from electrolyte to the cathode phase due to reactions (2.3) & (2.4) in cells 1 and 2. Each of these equations has the form:

$$a_{c1} + b_{c1} \ln(j(k')) - b_{c1} \ln \left(1 - \frac{j(k')}{j_{lim1}} \right) - V_{rc1} - a_{c2} - b_{c2} \ln(j(k'+1)) + b_{c2} \ln \left(1 - \frac{j(k'+1)}{j_{lim2}} \right) + V_{rc2} = 0 \quad (5.96)$$

where $k' = (k - (n-1)/2 + 1) + 2$ and k varies from $(n-1)/2 - 1$ to $(n-3)$

Of the remaining three equations, one is given by:

$$\begin{aligned}
 & \left(j(1) - j_{\text{sum1}} \left(\frac{st_b}{(n-1)/4} \right) \right) \left(\frac{t_{\text{perf}}}{k_{\text{perf}} \text{perf}} \right) + V_{\text{contact1}} + V_{\text{grafoil}} + a_a + \\
 & b_a \ln \left(j_{\text{sum1}} \left(\frac{st_b}{(n-1)/4} \right) \left(\frac{1}{(n-1)/4} \right) \left(\frac{1}{(1-\text{perf})} \right) \right) + V_{ra} - V_{rc1} + a_{c1} + \\
 & b_{c1} \ln(j((n-1)/2)) - b_{c1} \ln \left(1 - \frac{j((n-1)/2)}{j_{\text{lim1}}} \right) = 0
 \end{aligned} \tag{5.97}$$

where j_{sum1} is given by:

$$j_{\text{sum1}} = j(2) + j(3) + \dots + j((n-1)/2 + 1) \quad A \, m^{-2} \tag{5.98}$$

and V_{contact1} is the voltage drop due to contact between the grafoil and the graphite felt at the bipolar electrode and is given by:

$$V_{\text{contact1}} = \frac{j_{\text{sum1}}}{k_{a\text{contact}}} \quad V \tag{5.99}$$

and V_{grafoil} is the voltage drop due to the current transferred through the bipolar grafoil electrode and given by:

$$V_{\text{grafoil}} = \frac{j_{\text{sum1}} t_{\text{perf}}}{k_{\text{grafoil}}} \quad V \tag{5.100}$$

Equating the currents in the cathode bed of cell 1 to the total current on the anode (taking into account the area factor $(st_b)/((n-1)/4)$) gives us one more equation:

$$j(1) - j_{\text{sum2}} \left(\frac{st_b}{(n-1)/4} \right) = 0 \tag{5.101}$$

where

$$j_{\text{sum2}} = j((n-1)/2 + 2) + j((n-1)/2 + 3) + \dots + j(n) \quad A \, m^{-2} \tag{5.102}$$

The final (n^{th}) equation obtained by traversing the entire width of the reactor from the anode of cell 1 to the cathode of cell 2, is given by:

$$\begin{aligned}
 V_r - V_{ra} - a_a - b_a \ln(j(1)) - \frac{j(1)t_d}{k_{apd}} - \frac{j(1)t_b}{k_{apb}} + j_{sum1} \left(\frac{st_b}{(n-1)/4} \right) \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{1}{k_{apb}} \right) - \\
 \left(j(1) - j_{sum2} \left(\frac{st_b}{(n-1)/4} \right) \right) \left(\frac{t_{perf}}{k_{perf} perf} \right) - \frac{j(1)t_d}{k_{apd}} - \frac{j(1)t_b}{k_{apb}} + \\
 j_{sum3} \left(\frac{st_b}{(n-1)/4} \right) \left(\frac{t_b}{(n-1)/4} \right) \left(\frac{1}{k_{apb}} \right) - a_{c1} - b_{c1} \ln(j(n-1)) + b_{c1} \ln \left(1 - \frac{j(n-1)}{j_{lim1}} \right) \\
 + V_{rc1} - V_{contact2} = 0
 \end{aligned} \quad (5.103)$$

where $V_{contact2}$ is the voltage drop due to the contact between the end cathode and graphite felt and is given by:

$$V_{contact2} = \frac{j(1)}{k_{acontact}} \quad V \quad (5.104)$$

Also,

$$j_{add1} = ((n-1)/4 - 1)(j(2) + j(3)) + ((n-1)/4 - 2)(j(4) + j(5)) + \dots \quad A m^{-2} \quad (5.105)$$

$$(j((n-1)/2) + j((n-1)/2 + 1))$$

$$j_{add2} = j(2) + j(3) + \dots j((n-1)/2 + 1) \quad A m^{-2} \quad (5.106)$$

$$j_{add3} = ((n-1)/4 - 1)(j((n-1)/2 + 2) + j((n-1)/2 + 3)) + ((n-1)/4 - 2)(j((n-1)/2 + 4) + j((n-1)/2 + 5)) + \dots (j(n-1) + j(n)) \quad A m^{-2} \quad (5.107)$$

Material balance equations

The concentrations of perhydroxyl at the exit of the differential section for cells 1 and 2 in Figure 5.16 are given by:

$$C'_{1HO2-} = \left[C_{1HO2-} + \frac{w\Delta z \left(\left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{1HO2-} - \left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{1OH-} - i_{1HO2-} \right)}{2F liq/\rho_L} \right] kmol m^{-3} \quad (5.108)$$

$$C'_{2HO2-} = \left[C_{2HO2-} + \frac{w\Delta z \left(\left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{2HO2-} - \left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{2OH-} - i_{2HO2-} \right)}{2F liq/\rho_L} \right] kmol m^{-3} \quad (5.109)$$

The perhydroxyl ion concentration is then averaged using the following equation:

$$C'_{\text{HO}_2^-} = (C'_{1\text{HO}_2^-} + C'_{2\text{HO}_2^-})/2 \quad \text{kmol m}^{-3} \quad (5.110)$$

O_2 ($\mathbf{g}_2$ kg s ⁻¹)	O_2 ($\mathbf{g}_1$ kg s ⁻¹)
Electrolyte (liq kg s ⁻¹)	Electrolyte (liq kg s ⁻¹)
HO_2^- ($\mathbf{C}'_{2\text{HO}_2^-}$ kmol m ⁻³)	HO_2^- ($\mathbf{C}'_{1\text{HO}_2^-}$ kmol m ⁻³)
OH^- ($\mathbf{C}'_{2\text{OH}^-}$ kmol m ⁻³)	OH^- ($\mathbf{C}'_{1\text{OH}^-}$ kmol m ⁻³)
Na^+ ($\mathbf{C}'_{\text{Na}^+}$ kmol m ⁻³)	Na^+ ($\mathbf{C}'_{\text{Na}^+}$ kmol m ⁻³)
Temperature ($\mathbf{T}'$ K)	Temperature ($\mathbf{T}'$ K)
Reactor pressure ($\mathbf{P}'$ kPa)	Reactor pressure ($\mathbf{P}'$ kPa)

O_2 ($\mathbf{g}_2$ kg s ⁻¹)	O_2 ($\mathbf{g}_1$ kg s ⁻¹)
Electrolyte (liq kg s ⁻¹)	Electrolyte (liq kg s ⁻¹)
HO_2^- ($\mathbf{C}_{2\text{HO}_2^-}$ kmol m ⁻³)	HO_2^- ($\mathbf{C}_{1\text{HO}_2^-}$ kmol m ⁻³)
OH^- ($\mathbf{C}_{2\text{OH}^-}$ kmol m ⁻³)	OH^- ($\mathbf{C}_{1\text{OH}^-}$ kmol m ⁻³)
Na^+ ($\mathbf{C}_{\text{Na}^+}$ kmol m ⁻³)	Na^+ ($\mathbf{C}_{\text{Na}^+}$ kmol m ⁻³)
Temperature ($\mathbf{T}$ K)	Temperature ($\mathbf{T}$ K)
Reactor pressure ($\mathbf{P}$ kPa)	Reactor pressure ($\mathbf{P}$ kPa)

Figure 5.16 Differential section of Figure 5.11

The concentrations of perhydroxyl at the exit of the differential section for cells 1 and 2 are:

$$C'_{1\text{OH}^-} = \left[C_{1\text{OH}^-} + \frac{w\Delta z \left(\left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{1\text{HO}_2^-} + 3 \left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{1\text{OH}^-} - 2 i_{1\text{OH}^-} \right)}{2F \text{liq}/\rho_L} \right] \text{kmol m}^{-3} \quad (5.111)$$

$$C'_{2\text{OH}^-} = \left[C_{2\text{OH}^-} + \frac{w\Delta z \left(\left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{2\text{HO}_2^-} + 3 \left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{2\text{OH}^-} - 2 i_{2\text{OH}^-} \right)}{2F \text{liq}/\rho_L} \right] \text{kmol m}^{-3} \quad (5.112)$$

The hydroxyl ion concentration is then averaged using the following equation:

$$C'_{OH^-} = (C'_{1OH^-} + C'_{2OH^-})/2 \quad kmol\ m^{-3} \quad (5.113)$$

The sodium ion concentration does not change and is given by:

$$C'_{Na^+} = C_{Na^+} \quad kmol\ m^{-3} \quad (5.114)$$

The concentrations of perhydroxyl, hydroxyl and sodium ions calculated in equations (5.110), (5.113) and (5.114) are initialized again in the equations (5.115), (5.116) and (5.117), respectively, to allow voltage, material and energy balances over the next section of the reactor (Figure 5.11), i.e.,

$$C_{HO_2^-} = C'_{HO_2^-} \quad kmol\ m^{-3} \quad (5.115)$$

$$C_{OH^-} = C'_{OH^-} \quad kmol\ m^{-3} \quad (5.116)$$

$$C_{Na^+} = C'_{Na^+} \quad kmol\ m^{-3} \quad (5.117)$$

The oxygen flow exiting the differential section of Figure 5.16 is calculated by subtracting the oxygen used in reaction (2.3).

The O_2 generated in cell 2 is disengaged through the perforations and adds to the cell 1 flow rate. Accounting for this O_2 generation the O_2 flow rate in cell 1 is given by:

$$g'_1 = g_1 + \frac{M_{O_2} \left(\frac{i_{2HO_2^-}}{2} + \frac{i_{2OH^-}}{2} - \left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{1HO_2^-} \right) w \Delta z}{2F} \quad kg\ s^{-1} \quad (5.118)$$

$$g'_2 = g_2 - \frac{M_{O_2} \left(\left(\frac{st_b}{(n-1)/4} \right) \Sigma j_{2HO_2^-} \right) w \Delta z}{2F} \quad kg\ s^{-1} \quad (5.119)$$

The flow rate of O_2 is averaged for each incremental height as follows:

$$g' = (g'_1 + g'_2)/2 \quad kg\ s^{-1} \quad (5.120)$$

The O₂ flow rate must be reinitialized in order to carry out the voltage, material and energy balances on the next section (Figure 5.11) in the reactor, i.e.,

$$g = g' \quad \text{kg s}^{-1} \quad (5.121)$$

The oxygen generated on the anode of cell 1 is not accounted for in equation (5.119) as it flows through the dummy anode in Figure 5.11 and does not contribute to any further reactions in the reactor.

Energy balance equations

From Figure 5.16,

$$\text{heat input} + \text{heat generation} = \text{heat output} + \text{heat accumulation} \quad \text{kJ s}^{-1} \quad (5.122)$$

At steady state the accumulation term is zero therefore for 2 cells,

$$\text{heat output} - \text{heat input} = \left[2(\text{liq})c_l (T' - T) - \frac{1000 \left(\frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) (2g) \Delta H_{\text{evap}}}{M_{\text{O}_2}} \right] \text{kJ s}^{-1} \quad (5.123)$$

Neglecting entropy effects and sensible heat in the gas, the heat generation is approximated by:

$$\text{heat generation} = 0.001 (V_r + 2V_{\text{rc1}} - 2V_{\text{ra}}) j(1) w \Delta z \quad \text{kJ s}^{-1} \quad (5.124)$$

Equating equations (E-86) and (E-87) yields

$$T' = T + \frac{(0.001 (V_r + 2V_{\text{rc1}} - 2V_{\text{ra}}) j(1) w \Delta z)}{2(\text{liq})c_l} - \frac{1000 \left(\frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) (g) \Delta H_{\text{evap}}}{M_{\text{O}_2} (\text{liq})c_l} \quad \text{K} \quad (5.125)$$

where ΔH_{evap} is the heat of vaporization (42.85 kJ mol⁻¹ averaged from 273-373 K [Atkins, 1973]) for water.

The water vapour pressure P_{H_2O} is a function of temperature of the reactor and is calculated at the local temperature prevailing in the reactor with the assumption that the temperature does not significantly differ in two length increments in Figure 5.11.

The temperature is reinitialized for voltage, material and energy balances on the next section in the reactor by setting:

$$T = T' \quad K \quad (5.126)$$

The heat carried by O_2 is neglected as it contributes little to the overall heat balance.

Reactor pressure

The two phase pressure drop in the differential section (Figure 5.16) is given by:

$$\Delta P_{LG} = \nabla P_{LG} \Delta z \quad Pa \quad (5.127)$$

The new reactor pressure can be calculated by subtracting the pressure drop in the reactor from the original pressure:

$$P' = P - 0.001 \Delta P_{LG} \quad kPa \quad (5.128)$$

The pressure is then reinitialized for the voltage, material and energy balances on the next section (Figure 5.11) in the reactor according to:

$$P = P' \quad kPa \quad (5.129)$$

∇P_{LG} is calculated using equation (5.52) for the two-phase pressure gradient in the reactor.

Total reactor current

The reactor current is given by:

$$I_{\text{reactor}} = I_{\text{reactor}} + j(1)w\Delta z \quad \text{Amperes} \quad (5.130)$$

Current efficiency for peroxide generation and fraction current bypass

The current efficiency for perhydroxyl generation may be calculated from the following equation:

$$\text{C.E.} = \frac{2000F C_{\text{HO}_2^-}(\text{liq}/\rho_L)}{I_{\text{reactor}}} \quad (5.131)$$

The fraction current bypass (C.B.) is given by:

$$\text{C.B.} = \frac{I_{\text{reactor}} - w l_e \left(\sum_1^{\text{lin}} \Sigma j_{\text{HO}_2^-} - \sum_1^{\text{lin}} \Sigma j_{\text{OH}^-} \right)}{2I_{\text{reactor}}} \quad (5.132)$$

where $\sum_1^{\text{lin}} \Sigma j_{\text{HO}_2^-}$ and $\sum_1^{\text{lin}} \Sigma j_{\text{OH}^-}$ are the total currents for perhydroxyl generation and reduction respectively in cell 1 and are obtained using (5.88) and (5.90) and summing for the entire reactor.

Specific energy for peroxide generation

The specific energy for perhydroxyl generation may be calculated from the following equation:

$$\text{S.E.} = \frac{2FV_r}{2(3600)(34)\text{C.E.}} \quad \text{kWh kg}^{-1} \quad (5.133)$$

The solution algorithm for solving the two-cell reactor model is given in Figure 5.17. The code for solving the two-cell reactor model is given in Appendix E. The modelled results for the single-cell and two-cell reactor will be compared with the experimental results in Chapter 6.

Figure 5.17 Solution algorithm for the two-cell reactor model

CHAPTER 6

Experimental Results and Discussion

As has been discussed in Chapter 3, the objective of the present Thesis work is to explore the possibility of scaling up the perforated bipole electrochemical reactor for the generation of alkaline hydrogen peroxide. The perforated bipole electrochemical reactor was modelled for a single-cell and two cells (in series) in Chapter 5. Section 6.1 deals with the selection of the materials (anode, cathode and separator) for the reactor at hand. The bases for material selection have been previously discussed in Chapter 4. The results of the experiments conducted on those materials are discussed next.

6.1 Material selection

6.1.1 Anode

Various anode materials have been studied in the past at UBC for peroxide generation. These were monel, hastelloy C, platinized titanium, stainless steel 316 and nickel. Stainless steel (SS 316), because of its low cost and high corrosion resistance, was used as an anode material in most of the earlier work on the perforated bipole electrochemical reactor. A more thorough investigation of the anode materials was carried out as a part of the scale-up of this reactor in the present work.

6.1.1.1 Selection of anode material

Various combinations of anodes were tried in the small single-cell reactor as was discussed previously in Chapter 4. The experiments on a small single-cell were carried out under the following conditions:

- NaOH concentration: 1M

- NaOH flow rate: 20 ml/min
- Oxygen flow rate: 400 cc/min (STP)
- Diaphragm: RAI PHDC 120 (RAI material: radiation grafted polypropylene: thickness 0.5 mm, porosity 80%- no longer available)
- Pressure (reactor inlet): 125-100 kPa (abs.)

For anodes where perforation area and size are not specified:

- Perforation coverage area: 4%
- Perforation diameter: 1.6 mm

Of the various meshes selected to provide sufficient anode surface for electrolyte contacting, it was found that Ni mesh (40) (40 mesh per inch), Ni mesh (100) (100 mesh per inch) and Ni mesh (100) coated with porous nickel gave the best results in terms of the current efficiency and specific energy, as may be seen from Figures 6.1 and 6.2. Cells using Ni mesh (40) and Ni mesh (100) anodes gave lower specific energies than nickel mesh (100) coated with nickel. Uncoated nickel mesh (100) was therefore chosen as the anode material in subsequent experiments because it was cheaper than nickel mesh (40).

The trend of decreasing peroxide current efficiency with increasing superficial current density as observed in Figure 6.1, is seen in all the plots of peroxide current efficiency versus superficial current density. The decrease in current efficiency occurs largely due to the increased local overpotential in the graphite felt cathode that causes secondary reaction (2.4) to increase locally.

Raney nickel sprayed onto a stainless steel plate was also tried as an alternative to the Grafoil and mesh combinations. It was found that Raney nickel-based anodes could give significant benefit in terms of the specific energy; however, they were relatively poor in terms of the current efficiencies. The cost of fabricating these anodes in the laboratory was prohibitive as drilling perforations through nickel-plated steel was both tedious and expensive. Because of these considerations, Raney nickel was not investigated further as an anode material in the current work.

Figure 6.1 Peroxide current efficiency vs superficial current density for different anodes in the small single-cell reactor (other conditions as in section 6.1.1.1)

Figure 6.2 Specific electrical energy consumption for peroxide generation vs superficial current density for different anodes in the small single-cell reactor (other conditions as in section 6.1.1.1)

6.1.1.2 Investigating the possibility of better anode materials

It has been shown later (cf. Figure 6.18) that the ratio of Faradaic current to the bypass current decreases with increasing anode overpotential. Or to rephrase, the ratio of the current in the cell doing electrochemistry, to that bypassing through the perforations,

decreases with increasing anode overpotential. As one of the objectives of the present work is to minimize current bypass through the perforations in order to increase the current efficiency of the cell for peroxide generation, the choice of anode material is critical to the performance of the reactor. Therefore the possibility of a better anode material for the perforated bipolar electrochemical reactor was explored further. In that light, one such anode material that could better the reactor performance was thought to be NiCo_2O_4 . It is well known that the oxygen evolution overpotential (in alkaline condition) can be reduced using NiCo_2O_4 electrodes [Haennen et al., 1985]. These NiCo_2O_4 electrodes have importance in water electrolysis systems, where oxygen is evolved at the anode. With the intent of lowering the anode overpotential, NiCo_2O_4 was explored as a possible anode material. The preparation of NiCo_2O_4 electrodes is described in Chapter 4.

6.1.1.2a Testing the performance of NiCo_2O_4 bipolar electrode

Two experiments on the small two-cell reactor were conducted to test the effectiveness of the NiCo_2O_4 electrode. In the first experiment the bipolar electrode or the central electrode was chosen as nickel mesh coated with NiCo_2O_4 spinel oxide, while in the other an uncoated nickel mesh was used as the bipolar electrode with perforated Grafoil. The other parameters and conditions for running the two experiments were identical and are listed below:

- NaOH concentration: 1M
- NaOH flow rate: 40 ml/min
- Oxygen flow rate: 400 cc/min (STP)
- Diaphragm: SCIMat 700/20
- Pressure (reactor inlet): 901-875 kPa (abs.)

Anode perforation area and size:

- Perforation coverage: 4%
- Perforation diameter: 1.6 mm

Figure 6.3 Peroxide current efficiency vs superficial current density for small two-cell reactor with bipolar electrode coated with and without nickel cobaltate (NiCo_2O_4) (other conditions as in section 6.1.1.2a)

Figure 6.4 Specific energy vs current density for small two-cell reactor with bipolar electrode coated with and without nickel cobaltate (NiCo_2O_4) (other conditions as in section 6.1.1.2a)

The peroxide current efficiency and specific energy results versus current density, given in Figures 6.3 and 6.4, compare values on coated (with NiCo_2O_4) and uncoated nickel mesh anodes. It may be observed from Figure 6.3 that the current efficiency values are similar for the two cases for current densities greater than 3 kA m^{-2} . A plausible reason for these similar values is the fact that the ratio of Faradaic current to bypass current on the bipolar anode in the small two-cell reactor increases with current density. In the range $3\text{--}5 \text{ kA m}^{-2}$, a change in current density does not affect the ratio of Faradaic current to bypass current substantially and therefore no improvement in peroxide current efficiency is observed. Further, looking at Figure 6.4 it can be seen that the specific energy for the NiCo_2O_4 spinel oxide coated bipolar electrode is higher than that on the uncoated nickel mesh electrode for current densities greater than 2 kA m^{-2} . A plausible reason for the higher specific energy values for the reactor using the NiCo_2O_4 spinel

oxide coated bipolar electrode is that coating with this material causes the electrode to become more hydrophobic (less wettable), thereby preventing good liquid contacting. Poor liquid contacting results in an increased anode overpotential leading to high specific energies. Based on the above, further work on NiCo_2O_4 coated nickel mesh as an anode material was therefore discontinued.

6.1.1.2b Exploring the possibility of a novel bipole

Two different experiments were conducted on a novel kind of bipolar electrode. The aim of this study was to completely eliminate current bypass through the perforations. Current bypass, as was established in Chapter 5, occurs due to the electrolyte present in the perforations. However, the perforations are essential for the disengagement of oxygen. Thus, an ideal perforation would be one that allows the gas to disengage but not the liquid to pass through. With the intent of realizing such an electrode, an experiment was carried out by placing two porous polytetrafluoroethylene (PTFE) sheets between three strips of perforated Grafoil as described in section 4.2.1.2. The perforations in the central porous sheet (Figure 4.6) were filled with polystyrene beads. The conditions for operating the small two-cell reactor to test the PTFE layered bipolar electrode were:

- NaOH concentration: 1M
- NaOH flow rate: 40 ml/min ($6.6\text{e-}7 \text{ m}^3 \text{ s}^{-1}$)
- Oxygen flow rate: 400 cc/min ($6.6\text{e-}6 \text{ m}^3 \text{ s}^{-1}$) (STP)
- Diaphragm: SCIMat 700/20
- Pressure (reactor inlet): 900-875 kPa (abs.)

Anodes perforation area and size:

- Perforation coverage: 2 %
- Perforation diameter: 1.6 mm

The peroxide current efficiency and specific energy measured for this novel bipole are shown in Figures 6.5 and 6.6.

Figure 6.5 Peroxide current efficiency vs current density for small two-cell reactor with bipolar electrode with and without PTFE inserts (other conditions as in section 6.1.1.2b)

From Figure 6.5, it may be observed that the current efficiency for the small two-cell reactor using a PTFE-based bipolar electrode (Figure 4.4) is improved significantly compared with a perforated bipolar electrode without PTFE. The current efficiency difference between the two types of reactors (with and without PTFE inserts) decreases with increasing current density. The decrease in current efficiency difference is due to an increased ratio of Faradaic to bypass current with increasing current density.

Figure 6.6 Specific energy for peroxide generation vs current density for small two-cell reactor with bipolar electrode with and without PTFE inserts (other conditions as in section 6.1.1.2b)

The specific energy values for peroxide generation from a reactor with a PTFE-based bipolar electrode are also lower than those for the reactor without them (Figure 6.6). In essence, the use of a PTFE-based bipolar electrode improves the performance of the cell significantly, presumably by reducing the current bypass due to electrolyte while at the same time allowing the gas to disengage. Such electrodes could find future use in a scaled-up reactor generating alkaline peroxide. These electrodes may also offer a solution to other industrial electrochemical systems using bipolar electrodes where gas disengagement at one of the electrodes is an issue, and could be explored further in that light for individual electrochemical systems.

Further work on systems with bipolar electrodes using PTFE inserts was, however, discontinued because of the cost and complexity of the system.

Having explored various possible anode materials, uncoated nickel mesh (100) backed with perforated Grafoil was chosen as the anode material in the present work.

6.1.2 Diaphragm

Previous work at UBC employed a hydrophilic polypropylene based diaphragm as the separator material. This material with the trade name PHDC 120 (Radiation grafted polypropylene with thickness: 0.5 mm and porosity: 80 %) was obtained from PALL RAI Inc. Preliminary peroxide generation experiments were carried out using PHDC as the diaphragm. However, as the company closed down a few years ago, additional diaphragm material could not be obtained from that source. Therefore, an alternative material had to be found.

Various types of polypropylene diaphragms were tested for use as a separator material in the small single-cell reactor. These were obtained from SCIMAT, New Jersey. The grades of material that were tested were 700/20, 700/25, 700/28, 700/29, 700/74 (cf. Table 4.2). The plots of current efficiency and specific energy versus current density for different diaphragms are shown in Figures 6.7 and 6.8, respectively. The plots clearly show that SCIMAT 700/20 is the best material to work with as the current efficiency, in the current density range of importance $3\text{--}5\text{ kA m}^{-2}$, is the highest amongst all materials considered, and the specific energy is the least. Therefore SCIMAT 700/20 was chosen as the diaphragm material for the factorial runs discussed later in Chapter 6.

The experimental runs illustrated in Figures 6.7 and 6.8 with different diaphragms were carried out under the following conditions:

- NaOH concentration: 1M
- NaOH flow rate: $20\text{ cm}^3/\text{min}$ ($3.33\text{e-}7\text{ m}^3\text{ s}^{-1}$)
- Oxygen flow rate: $3.33\text{e-}6\text{ m}^3\text{ s}^{-1}$ (STP)
- Pressure (reactor inlet): 100-125 kPa (abs.)
- Anode: nickel mesh (100) & Grafoil
- Perforation coverage: 4%
- Perforation diameter: 1.6 mm

Experiments using SCIMAT 700/20 provided a high peroxide current efficiency on the small single-cell reactor, however the results using the same diaphragm on the medium single-cell reactor were poor. Therefore an alternative material was sought to obtain higher current efficiencies ($> 80\%$ at $1\text{-}5 \text{ kA m}^{-2}$) on the medium single-cell reactor. More recent work done using polyethylene diaphragms (EH-06A obtained from the Dutch company: DSM Solutech, Heerlens) has shown it to be superior to SCIMAT 700/20 (Table 4.3).

Since the experiments for comparing the performance between SCIMAT 700/20 and EH-06A were done on the medium-size single-cell reactor, the results for EH-06A are brought out later after the discussion on scale-up.

Figure 6.7 Peroxide current efficiency vs superficial current density for different diaphragms in the small single-cell reactor (other conditions as in section 6.1.2)

Figure 6.8 Specific energy for peroxide generation vs superficial current density for different diaphragms in the small single-cell reactor (other conditions as in section 6.1.2)

6.1.3 Cathode

As discussed in Chapter 2, the cathode material of choice in the present work is graphite felt. Scanning electron microscopy (SEM) was done for used and unused graphite felts by the Surface Science Western group, University of Western Ontario, to characterize the differences in surface morphology of the two graphite felts. These were obtained using a Hitachi S-4500 FESEM using a 10 kV electron beam and imaged with the lower chamber secondary electron detector. The SEM pictures of old (used) and new (unused) graphite felts obtained from Metaullics systems Inc., are shown in Figure 6.9a and 6.9b, respectively. The SEM images in Figures 6.9a and 6.9b, obtained at different

magnifications, clearly show the fibre structure of the felt samples. Closer examination of SEM images revealed that both the old and new graphite felts had similar gross fibre structures. The individual fibres were 20×10^{-6} m thick and they were made of smaller fibres or strands $3\text{--}5 \times 10^{-6}$ m thick. The only difference observed between the two samples was the presence of sodium-rich crystalline deposits on the old felt. This was due to its exposure to NaOH solutions.

Figure 6.9a Scanning Electron Microscopy for used graphite felts from Metaullic Systems Inc.

Figure 6.9b Scanning Electron Microscopy for unused graphite felts from Metaullic Systems Inc.

X-ray photoelectron spectroscopy was also done for the old (used) and new (unused) graphite felts to determine the surface carbon functionality. The XPS analysis was carried out with a Kratos AXIS Ultra X-ray photoelectron spectrometer. A monochromatized Al-K X-ray beam was used. The area analyzed was $\sim 700 \mu\text{m}$ by $300 \mu\text{m}$ in size. High resolution C(1s) spectra were obtained with 160 and 10 eV pass energies. A graphite sample (fractured in vacuum) was used to obtain a reference C(1s) graphite peak envelope. This reference peak was then used for subsequent fitting of the C(1s) peaks obtained from the felt samples. Figures 6.10aa & ab, 6.10ba & bb and 6.10ca & cb show the plots of surface functionality of various species (i.e. C, Na, Ca, O etc.) versus binding energy for reference graphite, old and new graphite felts, respectively. Table 6.1 summarizes the surface composition (atomic %) results and Table 6.2

summarizes the C(1s) peak deconvolution results that were used to determine the nature of the carbon in the graphite felts.

Figure 6.10aa Counts per second vs binding energy for reference graphite (fractured in vacuum)

Figure 6.10ab Counts per second vs binding energy for reference graphite (fractured in vacuum)

Figure 6.10ba Counts per second vs binding energy for old (used) graphite felt

Figure 6.10bb Counts per second vs binding energy for old (used) graphite felt

Figure 6.10ca Counts per second vs binding energy for new (unused) graphite felt

Figure 6.10cb Counts per second vs binding energy for new (unused) graphite felt

Table 6.1 XPS surface composition (atomic %)

Sample	Elements detected						
	C	O	Na	Ca	Cl	S	Si
Old GF	56.0	32.0	8.2	0.2	< 0.1	0.4	3.4
New GF	90.0	8.0	0.3	0.3	-	0.3	1.8
Reference graphite	99.0	1.0	-	-	-	-	-

Table 6.2 Analysis of C(1s) peak (results indicate area percentage of total carbon)

Sample	Graphitic carbon	Hydrocarbon (C-C, C-H)	Alcohol Ester (C-OH)	Ketone, Aldehyde Carbonyl (C=O)	Carboxylic acid carbonyl (C=O)	Carbonate O=(C=O)-O
Old GF	34.0	39.0	8.0	6.5	8.0	4.6
New GF	85.0	10.0	1.0	1.0	1.5	0.2
Reference graphite	100	-	-	-	-	-

It may be observed from the XPS studies (Table 6.1) that old graphite had only 56%_w surface carbon compared to 90%_w for new graphite felt. The low surface carbon content in the old graphite felts may be attributed to the presence of a high oxygen content (32%_w) due to their repeated use as a cathode, which allows oxygen to permanently occupy lattice sites in the carbon matrix. On inspection of the C(1s) peaks (Table 6.2), it was found that carbon was present in various oxidized forms, namely alcohols, esters, ketones, aldehydes, carboxylic acids and carbonates (Table 6.2). Also it was found that the outer surface of the new felt was comprised of ~ 85% graphite. The balance was hydrocarbon along with very small contributions from oxidized carbon groups. The old felt had only ~ 34% graphite functionality, and the balance was made up of hydrocarbon and oxidized forms of carbon.

The difference in oxidized carbon content for the old and new graphite felts may have an effect on the kinetics of the electroreduction of oxygen (reaction (2.3)). But how the kinetics translates into current efficiency changes is currently not clear. The kinetic data available in literature [Sudoh et al., 1985a] for the electroreduction of oxygen (reaction (2.3)) and reduction of perhydroxyl ions (reaction (2.4)) on carbon (EG-38, Nippon carbon) were used for modelling in the present work.

A sensitivity analysis of kinetics for reaction (2.3) and (2.4) is brought out in the end of this Chapter (section 6.3).

6.2 Reactor scale-up

The scale-up of the perforated bipole electrochemical reactor for the generation of alkaline peroxide was done in following steps:

- 1) Comparison of single and two-cell modelling results with experimental results for the small reactor
- 2) Factorial runs on the small two-cell reactor to determine the effect of perforation coverage and diameter
- 3) Scale-up of a single-cell reactor from small to medium size (scale-up philosophy: geometric, kinematic, thermal and current similarity, gas and liquid distribution)
- 4) Factorial runs on the medium two-cell reactor to determine the effect of perforation coverage and diameter
- 5) Comparison of the single-, two- and four-cell modelling results with experimental results for the medium reactor

6.2.1 Comparison of model predicted and experimental results for the small, single-cell reactor

The experimental results on the small single-cell are compared to the model predicted results in Figures 6.11, 6.12 and 6.13 (i.e. peroxide current efficiency, specific energy for peroxide generation and reactor outlet temperature respectively with superficial current density).

It may be observed from Figure 6.11 that an eddy diffusivity (D_{ed}) value of $2\text{e-}8\text{ m}^2\text{ s}^{-1}$ in the modelled results gives a closer fit to the experimental values at current densities exceeding 2.5 kA m^{-2} , whereas the eddy diffusivity value would lie between $1\text{e-}8$ and $2\text{e-}8\text{ m}^2\text{ s}^{-1}$ for a good fit of modelled and experimental current efficiencies for current densities in the range of $1\text{-}2.5\text{ kA m}^{-2}$. A plausible reason for the increasing eddy diffusivity value with increasing current densities is due to the increased rate of oxygen generation due to reaction (2.10) and (2.11) that causes a higher rate of liquid convection through the diaphragm, leading to an increase in the peroxide losses on the anode.

The experimental values for specific energy consumption for peroxide generation in Figure 6.12 are most near to the modelled values for an eddy diffusivity (D_{ed}) of $2\text{e-}8\text{ m}^2\text{ s}^{-1}$. The modelled specific energy values do not match the experimental values as the modelled voltages are lower than experimental voltages because of increased anodic overpotential with increasing current density. It is difficult to model the increasing anodic overpotential caused by the gas generation on the anode.

It may also be seen from Figure 6.13 that the experimental product outlet temperatures match the modelled temperatures quite well.

The experimental operating conditions for the single-cell reactor were:

- NaOH concentration: 1M
- NaOH flow rate: $25\text{-}30\text{ cm}^3/\text{min}$ ($4.1\text{e-}7\text{ - }5\text{e-}7\text{ m}^3\text{ s}^{-1}$)

- Oxygen flow rate: 200 cm³/min (6.6e-6 m³ s⁻¹) (STP)
- Diaphragm: SCIMAT 700/20
- Pressure (reactor inlet/outlet): 900/875 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2 %
- Perforation diameter: 1.6 mm

Figure 6.11 Peroxide current efficiency versus superficial current density for small single-cell reactor for modelled and experimental runs (other conditions as in section 6.2.1)

Figure 6.12 Specific energy for peroxide generation versus superficial current density for small single-cell reactor for modelled and experimental runs (other conditions as in 6.2.1)

Figure 6.13 Reactor product outlet temperature versus superficial current density for small single-cell reactor for modelled and experimental runs (other conditions as in section 6.2.1)

6.2.2 Comparison of model predicted and experimental results for the small, two-cell reactor

The experimental results on the small two-cell are compared to the model predicted results in Figures 6.14, 6.15 and 6.16 (i.e. peroxide current efficiency, specific energy for peroxide generation and reactor outlet temperature respectively with superficial current density).

The modelled peroxide current efficiency values are close to the experimental values for eddy diffusivity (D_{ed}) in the range of $1\text{--}2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at current densities $< 2.5 \text{ kA m}^{-2}$, whereas it may be in the range of $2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at current densities $> 2.5 \text{ kA m}^{-2}$. These results are in line with the single-cell results discussed previously in section 6.2.1.

The experimental values for specific energy consumption for peroxide generation in Figure 6.15 are most near to the modelled values for an eddy diffusivity (D_{ed}) of $2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The modelled specific energy values do not match the experimental values as the modelled voltages are lower than experimental voltages because of increased anodic overpotential with increasing current density. It is difficult to model the increasing anodic overpotential caused by the gas generation on the anode.

It may also be seen from Figure 6.16 that the experimental product outlet temperatures match the modelled temperatures quite well.

The experimental conditions for operating the small two-cell reactor were:

- NaOH concentration: 1M
- NaOH flow rate: $35\text{--}40 \text{ cm}^3/\text{min}$ ($5.8 \times 10^{-7} \text{--} 6.6 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$)
- Oxygen flow rate: $300 \text{ cm}^3/\text{min}$ ($5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$) ((STP))
- Diaphragm: SCIMAT 700/20
- Pressure (reactor inlet/outlet): 900/875 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2 %

- Perforation diameter: 1.6 mm

Figure 6.14 Peroxide current efficiency versus superficial current density for small two-cell reactor for modelled and experimental runs (other conditions as in 6.2.2)

Figure 6.15 Specific energy for peroxide generation versus superficial current density for small two-cell reactor for modelled and experimental runs (other conditions as in 6.2.2)

Figure 6.16 Reactor outlet temperature versus superficial current density for small two-cell reactor for modelled and experimental runs (other conditions as in 6.2.2)

The current efficiencies obtained in the present work in experiments on the small two-cell reactor were much lower than that required to obtain a scaled-up reactor with viable current efficiency (ca. 75 % at $> 3 \text{ kA m}^{-2}$). The low current efficiencies in the experimental work described above were largely due to the lack of the availability of a good diaphragm (i.e a high D_{ed} value). The possibility of a better diaphragm material was explored but a suitable diaphragm could not be obtained during the initial stages of the Thesis. Therefore polypropylene (SCIMAT 700/20) was used as the diaphragm material in the first set of experiments on the medium reactor.

6.2.3 Factorial experiments

Factorial experiments were carried out on both the small and medium reactor in an attempt to find the optimal perforation diameter and perforation coverage for the perforated bipole electrochemical reactor. A 2^2 factorial design was employed for both two-cell reactors (small and medium) as shown in Figure 6.17. The two independent variables chosen were the perforation diameter (0.8 mm and 1.6 mm) and perforation coverage (2 & 4%). These variables were chosen from the preliminary experiments which showed that a perforation coverage less than 2% is insufficient to disengage oxygen and leads to cell burn out. On the other hand any coverage greater than 5% leads to a high loss in current efficiency due to current bypass. Also the perforation diameters selected were 0.8 mm and 1.6 mm. The perforation diameter of 1.6 mm was selected on the basis of past experience and could be increased in future work. However, increasing the diameter by more than a factor of two would reduce the number of perforations more than four times and cause a problem in oxygen disengagement.

Figure 6.17 2^2 factorial design for two-cell reactor

6.2.4 Factorial experiments on the small two-cell reactor

The results of the factorial runs for the small two-cell reactor are given in Tables G.1 to G.5 (Appendix G). The main, interaction and curvature effects of perforation coverage and diameter on current efficiency are given in Table 6.3.

The conditions for operating the small two-cell reactor were:

- NaOH concentration: 1M
- NaOH flow rate: 35-50 cm³/min (6.6e-7 – 8.3e-7 m³ s⁻¹)
- Oxygen flow rate: 400 cm³/min (6.6e-6 m³ s⁻¹) (STP)
- Diaphragm: SCIMAT 700/20
- Pressure (reactor inlet/outlet): 900/875 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2-4 %
- Perforation diameter: 0.8-1.6 mm

Table 6.3 Effect of perforation coverage and perforation diameter on the current efficiency for the 2² factorial design on small two-cell reactor

Current density kA m ⁻²	Main effect due to perforation coverage %	Main effect due to perforation diameter %	Interaction effect due to perforation coverage & diameter %	95% confidence interval	Curvature effect %	95% confidence interval
0.33	-14.0	4.5	-0.7	± 7.7	0.5	± 7.3
1.00	-6.7	6.4	3.7	± 8.2	-0.7	± 7.8
2.33	-8.4	6.5	4.2	±16.8	-2.7	±16.1
3.00	-6.5	6.8	3.0	±14.1	-2.4	±13.5
3.66	-5.1	6.8	1.4	±11.0	-5.7	±10.5
4.00	-2.8	7.3	1.8	± 9.9	-4.3	± 9.5
4.66	-2.1	7.0	0.8	±11.0	-3.4	±10.5
5.00	-1.2	4.8	0.8	±11.3	-4.3	±10.8

6.2.4.1 Effect of perforation coverage on current efficiency

Table 6.3 shows the effect of perforation coverage and perforation diameter on the current efficiency for a two-cell 2^2 factorial experimental run on the small reactor. It may be seen that an increased perforation coverage results in a decrease of current efficiency by 14.0% at 0.33 kA m^{-2} to 1.2% at 5 kA m^{-2} . This trend shows that current efficiency decreases with increasing perforation coverage for any value of current density. Figure 5.15 provides the physical explanation of these results and shows that at the bipolar electrode, there are two resistances that decide the path for the current flow. One of these is the resistance due to the electrochemical reactions ((2.3) and (2.4)) and the other is due to the perforation conductance, k_{perf} . As the current density increases, the resistance due to the electrochemical reactions ((2.3) and (2.4)) reduces in comparison to the fixed resistance (conductance k_{perf}) of the electrolyte. This increases the ratio of Faradaic current to bypass current through the bipolar electrode. So the effect of the increased perforation coverage becomes less important with an increase in current density.

It may be seen from Table 6.3 that the confidence interval at certain current densities is high (e.g. $\pm 16.8\%$ at 2.33 kA m^{-2}) whereas the main effect is less than the confidence interval (-8.4% at 2.33 kA m^{-2}). A higher value of the confidence interval than the main effect indicates that nothing can be concluded from the main effect, however, the trend of decreased current efficiency difference with increasing current density is real and has been explained from the model in section 6.2.4.5.

6.2.4.2 Effect of perforation diameter on current efficiency

Table 6.3 also shows the effect of perforation diameter on the current efficiency of a small two-cell reactor. It may be observed that the effect of increased perforation diameter is always positive at any current density value ($+ 4.5\%$ at 0.33 kA m^{-2} to $+4.8\%$ at 5 kA m^{-2}). These results may be explained by the fact that an increased perforation diameter leads to decreased capillary pressure in the perforations. Capillary pressure is the pressure caused by the liquid in the perforations. The gas has to overcome less force

or do less work in order to disengage through the perforations, resulting in decreased gas hold-up on the nickel mesh anode (Figure 5.11). A decrease in gas hold-up increases the wetting efficiency of the nickel mesh anode that leads to low oxygen overpotential at the anode. Increased wetting or better electrolyte contacting increases the ratio of Faradaic current to bypass current, thereby resulting in increased current efficiency. This effect of perforation diameter on the current efficiency has only been explained qualitatively. Unfortunately this parameter is extremely difficult to model due to the lack of a good understanding of the flow mechanism of gas and liquid through the perforations.

6.2.4.3 Interaction of perforation coverage and perforation diameter

Interaction here implies the combined effect of increased perforation coverage (2 to 4 %) and perforation diameter (0.8 to 1.6 mm).

Looking at the interaction values in Table 6.3, it may be observed that they first increase with current density (- 0.7% at 0.33 kA m^{-2} to 3.0 % at 2.33 kA m^{-2}). This may be explained by the fact that at low current density (0.33 kA m^{-2}), the gas hold-up on the nickel mesh anode is low due to a lower rate of oxygen generation. At lower perforation diameter the gas has to overcome a higher capillary pressure causing the interaction effect to be more dependent on the perforation diameter. Increasing the perforation diameter from 0.8 mm to 1.6 mm leads to lower capillary pressures and reduced gas hold-ups, resulting in improved wetting of the nickel mesh anode. Increased wetting of the nickel mesh anode causes lower overpotentials (therefore lower fractional current bypass through the perforations) resulting in increased current efficiency.

On the other hand increasing the current density further (from 2.33 to 5 kA m^{-2}) leads to a decrease in the interaction effect. A plausible reason for this is that the gas hold-up in the anode is high enough at 2.33 kA m^{-2} that the effect of increased perforation coverage becomes more important, resulting in decreased current efficiency.

6.2.4.4 Curvature

The curvature is the difference between the centre point and the average of the factorial points. Physically the curvature indicates the degree of non-linearity in the system under consideration.

The curvature effect on the small two cell reactor as seen from Table 6.3 is statistically insignificant which suggests that there is no non-linearity in the system over the range of perforation coverages and diameters studied here.

6.2.4.5 Comparison of experiments and model for small two-cell reactor

Figure 6.18 shows the results of current bypass fraction for the small two-cell reactor based on the model. The figure demonstrates that the difference between the current bypass fractions for 4% and 2% perforation coverages are greater at low current density than at high current density. The decrease in the current bypass fraction difference results from the increasing ratio of Faradaic current to bypass current with increasing current density. In Table 6.3 a similar trend to that discussed previously in section 6.2.4.1 may be seen, that is, the effect of perforation coverage on current efficiency decreased with increasing current density.

The aim of the model is to guide the experiments to scale-up the reactor. The trends of current bypass fraction based on the model (Figure 6.18) and on the factorial experiments are in consonance with one another. Further, the effect of perforation coverage on current efficiency was not understood previously. These results are sufficient to establish a better physical understanding of how the perforated bipole electrochemical reactor works. Armed with this new understanding of oxygen gas disengagement from the anode and the bipole electrode function, the scale-up of the reactor was attempted.

More importantly, it is clear from the factorial experiments that a low perforation coverage and large perforation diameter provides the best current efficiencies amongst all

the factorial and centre points. So a perforation diameter of 1.6 mm diameter and perforation coverage of 2% were selected as the most suitable configuration for the scale-up work.

Figure 6.18 Current bypass versus superficial current density for small two-cell reactor (model prediction)

6.2.5 Scaling-up from small single-cell to medium single-cell reactor

Before discussing the scale-up issue it is worth reconsidering the title of the Thesis project. It uses the word trickle bed. Trickle bed usually implies a co-current flow of gas and liquid in the downward direction. This kind of flow has gas as the continuous phase and liquid as the dispersed phase. The peroxide process operates in the limit where there is a transition from a liquid continuous to a gas continuous regime. Trickle flow provides a very high gas to liquid mass transfer capacity and low pressure drop and therefore was chosen by Oloman (1979) as the mode of flow through the reactor. As the peroxide generation process at high current density is mass transfer limited, therefore it is necessary to choose a process that would maximize the mass transfer limited current

density. The gas to liquid mass transfer capacity can be increased by choosing a flow configuration from bottom to top instead of top to bottom [Hodgson and Oloman, 1999]. This bottom to top approach increases the mass transfer at the cost of increased pressure drop and has therefore been chosen as the flow mode in the present work (it may also increase liquid hold-up with consequent higher effective conductivity/electrolyte in bed).

6.2.5.1 Scale-up philosophy

The philosophy of scaling-up is to ensure that corresponding variables of the two reactors are similar. Various similarity criteria are defined to guide the engineer to efficiently scale-up a reactor. The criteria normally employed in thermochemical reactors are geometric, kinematic and thermal similarity between the reactors. However, in the case of electrochemical reactors an additional criterion necessary to fully define the scale-up parameters is the current/potential similarity. These parameters are discussed below:

Geometric similarity

Geometric similarity is achieved by fixing the dimensional ratios of the corresponding reactors. However, for electrochemical reactors, this criterion cannot normally be met as increasing the inter-electrode gap would cause a high voltage drop and increased energy costs. Also in 3D electrodes an increased electrode thickness may cause a decrease in the average potential driving force or promote secondary reactions (cf. Chapter 2). Therefore, geometric similarity in electrochemical reactors is usually ignored. Scale-up in electrochemical reactors is achieved by using multiple cells and reactor units [Goodridge and Scott, 1994].

Kinematic similarity

Kinematic similarity is concerned with the flow velocities within a system. In any reactor, the gas and liquid flow loads or more generally the Reynolds number govern the pressure drop, liquid and gas hold-up and more importantly the mass transfer coefficients

in the system. Therefore it is necessary to maintain a close similarity of gas and liquid flow velocities through the corresponding reactors. In the present work, a liquid flow of 20-25 cm³/min ($3.3\text{e-}7 - 4.16\text{e-}7 \text{ m}^3 \text{ s}^{-1}$) was used for the small reactor per cell having a cross-sectional flow area of 3.2 mm by 25 mm i.e. 80 mm². To maintain a similar velocity for the liquid flow in the medium reactor per cell (cross-sectional flow area equal to 3.2 mm by 40 mm i.e. 128 mm²), a liquid flow rate in the range 32-40 cm³/min ($5.3\text{e-}7 - 6.6\text{e-}7 \text{ m}^3 \text{ s}^{-1}$) is desired. The flow rate selected in the present reactor is close to this value and was 40-45 cm³/min ($6.6\text{e-}7 - 7.4\text{e-}6 \text{ m}^3 \text{ s}^{-1}$).

Gas loads in the present work are more dependent on the stoichiometric requirements (reaction (2.3)) than by the kinematic similarity criterion. Oxygen flow rates in the small reactor were $\sim 200 \text{ cm}^3/\text{min}$ ($3.3\text{e-}6 \text{ m}^3 \text{ s}^{-1}$ (STP)), whereas for the medium reactor they were in the range 300-400 cm³/min ($5\text{e-}6 - 6.6\text{e-}6 \text{ m}^3 \text{ s}^{-1}$ (STP)).

Thermal similarity

Thermal similarity implies that the temperatures in the corresponding portions of the reactors under comparison be identical. This criterion is difficult to maintain in thermochemical reactors and even more so in electrochemical reactors. In a bipolar configuration, providing cooling channels between cells is not only difficult but also expensive and may defeat the purpose of scale-up (i.e. in lowering the cost of product generation).

Current similarity

Electrochemical reactors, unlike their thermochemical counterparts, require electrical similarity and it is usually the most important criterion in the scale-up of such reactors. Electrical similarity exists between two units when corresponding electrode potential and current density differences bear a constant ratio [Goodridge and Scott, 1994]. The criterion necessitates a constant inter-electrode gap on scale-up. One factor normally employed to quantify the effect is the Wagner number which may be defined as

$$Wa = \left(\frac{k_{apl}}{L'} \right) \left(\frac{dV'}{di'} \right) \quad (6.1)$$

where k_{apl} is the electrolyte conductivity, V' the electrode potential, i' the current density and L' the characteristic length. So, for electrical similarity, the Wagner number in the two reactors should have the same value at all points being compared.

In the case of a peroxide reactor this criterion is met to some degree as the inter-electrode gap is the same for both the small and medium reactor (3.2 mm); however, electrolyte conductivity may differ because of the higher temperatures in the medium reactor.

Of the four criteria (geometric, kinematic, thermal and current similarity) discussed above, only the kinematic similarity is maintained and the current similarity for the two electrochemical reactors maintained to some extent. The difference in current similarity, for reactors of different sizes, occurs largely due to the increased electrolyte conductivity and larger peroxide concentrations in the small and medium reactors. From this it may be inferred that the use of similarity criterion is not the best approach for scaling-up electrochemical reactors. Therefore a better and more prudent way to scale-up electrochemical reactors is to model the reactor at hand and then compare the reactor performances in terms of product current efficiency, specific energy, temperature, etc.

For the above reason the scale-up of the present reactor was attempted by first modelling the small and medium reactor and then comparing the predicted results with the experimental results.

Another important issue in scale-up is the gas and liquid distribution within a cell and it is discussed in the following section.

Gas and liquid distribution

Gas and liquid flow distribution is one of the major problems when scaling-up an electrochemical reactor. The flow was visualized on the cathode bed of a small reactor by placing the graphite felt between two perspex glass sheets and passing the gas and liquid flow from bottom to top (cf. Chapter 4). Gas and liquid flowed in the form of slugs. Slugs of liquid were observed to flow over the graphite felt cathode with gas flowing intermittently between the slugs. The liquid slugs were uniform throughout the length (120 mm) of reactor covering the entire width (25 mm).

Flow distribution visualization experiments similar to those in the small reactor were carried out on the medium reactor using a straight cut graphite felt as shown in Figure 6.19. These experiments were carried out at 125 kPa gauge (inlet pressure). The O_2 requirement at 5 kA m^{-2} (maximum used in the present work) was $420 \text{ cm}^3/\text{min}$ ($7\text{e-}6 \text{ m}^3 \text{ s}^{-1}$ (STP)) or $50 \text{ cm}^3/\text{min}$ ($8.3\text{e-}7 \text{ m}^3 \text{ s}^{-1}$ at 900 kPa abs.: 1.25 times stoichiometric for O_2 as the limiting reactant). The scaled-up reactor was intended to operate at 900 kPa abs., so the volumetric flow rate of oxygen chosen at 100 kPa for visualizing the flow was varied from 50 to $200 \text{ cm}^3/\text{min}$ ($8.3 \text{ e-}7$ – $3.33 \text{ e-}6 \text{ m}^3 \text{ s}^{-1}$)(STP). It was observed that at approximately $1/5^{\text{th}}$ the length of reactor for a gas flow of $50 \text{ cm}^3/\text{min}$ ($8.3 \text{ e-}7 \text{ m}^3 \text{ s}^{-1}$) and liquid flow of $40 \text{ cm}^3/\text{min}$ ($6.6 \text{ e-}7 \text{ m}^3 \text{ s}^{-1}$), the liquid and gas flows became segregated as is shown schematically in Figure 6.20. At this point, the gas or oxygen began flowing through the centre and the liquid or electrolyte along the sides of the graphite felt. This led to poor contacting between the three phases (gas-liquid-solid). Any place on the electrode where there is no liquid contact means there is no flow of current and hence poor current distribution. Good 3-phase contacting is essential for the performance of the reactor as the gas needs to diffuse through the electrolyte or liquid film and react at the graphite felt surface together with water to produce perhydroxyl ions. This type of contacting was not possible on the scaled-up straight cut cathode shown in Figure 6.19. After several trials using different cathode configurations it was found that constrictions were needed in the cathode (see Figure 6.19), so that the gas and liquid could redistribute and maintain good contacting.

Figures 6.21 and 6.22 show the results of experiments for current efficiency and peroxide concentration on a small single-cell reactor and medium single-cell reactor with straight cut and constricted cathodes. These experiments were done under the following conditions:

- NaOH concentration: 1M
- NaOH flow rate:
small cell: $25 \text{ cm}^3/\text{min}$ ($4.1\text{e-}7 \text{ m}^3 \text{ s}^{-1}$)
medium cell: $55 \text{ cm}^3/\text{min}$ ($9.1\text{e-}7 \text{ m}^3 \text{ s}^{-1}$)
- Oxygen flow rate: $300 \text{ cm}^3/\text{min}$ (STP)
- Diaphragm: SCIMAT 700/20
- Pressure(reactor inlet/outlet): 900/875 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2 %
- Perforation diameter: 1.6 mm

Figure 6.19 Cathode shapes

Figure 6.20 Flow distribution of gas and liquid through graphite felt cathodes

It may be observed from Figure 6.21 that the current efficiency at 0.5 kA m^{-2} was higher (67%) for a straight cut cathode compared to the constricted cathode (59.8%). However, with increased current density, the current efficiency for a straight cut cathode dropped much more rapidly in comparison to the constricted cathode. At 5 kA m^{-2} , the efficiency for the straight cut cathode was only 26.8% as opposed to a value of 57.4% for a constricted cathode. This is a significant gain in efficiency and is due to a more even

flow of gas and electrolyte through the cathode bed in the constricted cathode cell that allows better gas-liquid-solid contacting compared to the straight cut cathode cell.

Also the constricted cathode may be compared to the small single-cell reactor experiment. The results show that the current efficiency (85%) at the starting current density (1 kA m^{-2}) for the small single-cell is much higher than the corresponding efficiency (63%) for the medium single-cell. However the efficiencies approach similar values at current densities exceeding 3 kA m^{-2} (65.4% for the medium cell and 68.8% for small cell at 3 kA m^{-2}).

Figure 6.21 Comparison of current efficiencies for small single-cell reactor and straight cut & constricted cathodes for medium single-cell reactor (other conditions as in section 6.2.5)

The reason for this current efficiency difference between the two reactors (small and medium) at low current densities is due to the loss of perhydroxyl ions through the diaphragm. In the small reactor the concentration of perhydroxyl ions exiting the reactor is relatively low compared with the exit concentration of perhydroxyl ions for medium-sized reactor with similar current density. At low concentrations the loss through the

diaphragm due to convection is also less and therefore the current efficiency is high. As the current density increases in the small reactor so does the perhydroxyl concentration leading to decreased current efficiencies for perhydroxyl formation. At current densities $> 3 \text{ kA m}^{-2}$, the efficiency for both the reactors are comparable because of mass transfer constraints. So the constricted cathode gives a better scaled-up medium cell.

Figure 6.22 Comparison of peroxide concentration for small single-cell reactor and straight cut & constricted cathodes for medium single-cell reactor (other conditions as in section 6.2.5)

Another problem associated with the scale-up is the non-uniform gas hold-up in the cathode and the anode. Gas hold-up usually increases in the reactor from bottom to top. With increased gas hold-up the effective conductivity of the electrolyte decreases, shifting increased current densities to the lower section of the reactor. Lower current densities on the upper section of the reactor results in increased current bypass in the upper section of the reactor. As the peroxide concentration is higher in the upper section, an increased current bypass can lower the peroxide current efficiency. Also increased gas hold-up would increase the axial fluid dispersion that may further lower the peroxide current efficiency. Efficient running of the commercial perforated bipole electrochemical

reactor may therefore require a modification in the design such as manipulating the cathode and diaphragm along the reactor.

6.2.6 Factorial experiments on the medium two-cell reactor

Based on the medium single-cell scaled up reactor, 2^2 factorial runs as discussed previously (cf. section 6.2) for small a two-cell reactor, were also done for the medium reactor. The detailed results of the factorial runs for the small two-cell reactor are given in Tables G.6 to G.10 (Appendix G). The analysis of the factorial runs are given in Table 6.4.

Table 6.4 Effect of perforation coverage and perforation diameter on the current efficiency for the 2^2 factorial design on a medium two-cell reactor

Current density kA m^{-2}	Main effect due to perforation coverage %	Main effect due to perforation diameter %	Interaction effect due to perforation coverage & diameter %	95% confidence interval for main and interaction effects %	Curvature effect %	95% confidence interval for curvature effect %
0.5	0.2	-0.3	2.9	± 4.5	-1.9	± 4.3
1.0	0.2	-0.1	-0.3	± 5.4	-1.2	± 5.2
1.5	-1.3	0.2	0.5	± 6.3	-3.2	± 6.0
2.0	-2.8	2.6	-2.2	± 8.4	-3.1	± 8.0
2.5	-3.2	0.6	-4.4	± 9.2	-8.0	± 8.8
3.0	-4.8	-1.2	-6.5	± 7.3	-7.9	± 7.0
3.5	-6.9	1.5	-4.3	± 8.3	-4.3	± 7.9
4.0	-5.9	3.2	-3.6	± 6.6	-4.1	± 6.3
4.5	-7.1	4.0	-1.4	± 5.7	-2.9	± 5.4

Factorial experiments on the medium two-cell reactor were conducted under the following conditions:

- NaOH concentration: 1M
- NaOH flow rate: 85-95 cm³/min (1.4e-6 – 1.6e-6 m³ s⁻¹)
- Oxygen flow rate: 600 cm³/min (1e-5 m³ s⁻¹)(STP)
- Diaphragm: SCIMAT 700/20
- Pressure(reactor inlet/outlet): 900/600 kPa abs.
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2-4 %
- Perforation diameter: 0.8-1.6 mm

6.2.6.1 Effect of perforation coverage on current efficiency

It may be observed from Table 6.4 that at lowest current densities (0.5-1 kA m⁻²) there is no effect of increased perforation coverage on the current efficiency. The change in current efficiency value at 0.5 kA m⁻² is 0.2%. That means there is no change in current efficiency with increased perforation coverage. This is because the gas hold-up on the nickel mesh anode and in the perforations is too high to allow any current bypass through the perforations. However, as the current density increases, the effect of increased perforation coverage becomes more visible. That is the current efficiency decreases much more at 4.5 kA m⁻² (-7.1%) than at 1.5 kA m⁻² (-1.3%) when the perforation coverage is increased from 2 to 4%. This result is contrary to those obtained from modelling and also the experimental results for the small reactor (section 6.2.4.1).

These differences can be explained by the fact that as the current density in the medium two-cell reactor is increased, more oxygen is produced on the nickel mesh anode due to reactions (2.10) and (2.11). Oxygen generated on the anode, when not able to disengage at a sufficient rate, obscures the nickel mesh surface and lowers the wetting efficiency of the nickel mesh anode. Correspondingly the proportion of perforation coverage increases. So these perforations become a source of current bypass at current densities exceeding 1 kA m⁻². This explanation is supported by the fact that the nickel mesh anode was generally found to be “burnt out” after two or three experiments on the medium-sized reactor. Diaphragm burn-out occurs when the generated oxygen is not able

to disengage properly from the anode, causing a maldistribution of electrolyte on the nickel mesh anode. This maldistribution of electrolyte leads to very high local current densities and causes high local temperatures that result in pin-hole burns on the cathode. Once pin-hole burns are established they exacerbate the problem by allowing current short circuiting which eventually leads to diaphragm burn-out.

It may be seen from Table 6.3 that the confidence interval at certain current densities is high (e.g. $\pm 8.8\%$ at 2.33 kA m^{-2}) whereas the main effect is less than the confidence interval (-3.2 at 2.33 kA m^{-2}). A higher value of the confidence interval than the main effect indicates that nothing can be concluded from the main effect, however, this trend of increased current efficiency difference with increasing current density has been observed for a number of replicated experiments and so the trend is assumed to be real.

6.2.6.2 Effect of perforation diameter on current efficiency

Table 6.4 shows the main effect of perforation diameter on current efficiency with current density. It may be observed that current efficiency increases with increased perforation diameter (0.8 to 1.6 mm) for most current density values. The increased current efficiency for a positive change in perforation diameter may be attributed to the relatively lower gas hold-up for a larger perforation diameter. Low gas hold-up allows better electrolyte contacting with the anode surface thereby increasing the ratio of Faradaic to bypass current. These results for the effect of perforation diameter are consistent with the small two-cell reactor results (section 6.2.4.2). For current density values for which the current efficiency decreases with increased perforation diameter, the effect is not appreciable ($> -1.2\%$). This negative value is insignificant.

6.2.6.3 Interaction of perforation coverage and perforation diameter

The interaction effect of perforation coverage and perforation diameter for the medium reactor is different from that on the small reactor. Here contrary to the results on

the small two-cell reactor (section 6.2.4.3), the interaction effect on current efficiency decreases initially with current density (2.9 % at 0.5 kA m^{-2} to -6.5 % at 3 kA m^{-2}) and then increases with current density (-6.5 % at 3 kA m^{-2} to -1.3 % at 5 kA m^{-2}). The increasing trend in current efficiency with current density is because the gas hold-up at 0.5 kA m^{-2} is sufficient to cause a maldistribution of electrolyte on the nickel mesh anode. At the lower perforation diameter of 0.8 mm, the maldistribution is worse due to higher gas hold-up than at a perforation diameter of 1.6 mm. The electrolyte maldistribution causes a lower wetting efficiency of the nickel mesh anode that results in increased fractional current bypass through the perforations at lower perforation diameter (0.8 mm).

On the other hand, in the high current density range ($3\text{-}5 \text{ kA m}^{-2}$), the current efficiency is not substantially influenced by current density because of the decreasing ratio of Faradaic current to bypass current with increasing current density. With an increase in perforation diameter, the gas hold-up on the nickel mesh anode is lowered, resulting in better anode wettability and less electrolyte maldistribution. Better electrolyte distribution and anode contacting lowers the bypass current and results in increased current efficiency.

6.2.6.4 Curvature

The curvature effect on the medium two-cell reactor as seen from Table 6.4 is mostly statistically insignificant which suggests that there is no non-linearity in the system.

6.2.6.5 Scaled-up medium reactor configuration

From the experiments on the medium two-cell reactor, it may be inferred that a low perforation coverage and high perforation diameter would provide a high current efficiency for peroxide generation. From the experiments in the present work, 2 % was the lowest perforation coverage used and 1.6 mm was the highest perforation diameter.

So these are chosen as the values that define the configuration of perforations for the scaled-up medium reactor.

6.2.6.6 Comparison of model predictions with experimental results for a medium two-cell reactor

The experiments discussed so far in Chapter 6 were carried out using the polypropylene diaphragm (SCIMAT 700/20). This diaphragm as was explained earlier (section 6.3) allows a high peroxide loss on the anode probably due to significant electrolyte convection through the diaphragm. However, in order to create a scaled-up reactor that has commercial potential, a better diaphragm had to be found. A small pore size ($< 10\text{e-}6$ m), stability in strong alkaline solutions and a high degree of wettability (hydrophilic) were some of the properties that the diaphragm was required to possess to be a good candidate for its use in the peroxide reactor. Such a material was found (micro-porous polyethylene-DSM Solutech, Netherlands: cf. Chapter 4) and experiments were conducted on it using a 2% perforation coverage and 1.6 mm perforation diameter in both medium single- and two-cell reactors.

The conditions for operating the reactor were:

- NaOH concentration: 1-2 M
- Diaphragm: (SCIMAT 700/20 and SOLUPOR EH-06A)
- NaOH flow rate:
 - single-cell: $40\text{-}50\text{ cm}^3/\text{min}$ ($6.6\text{e-}7$ - $8.3\text{e-}7\text{ m}^3\text{ s}^{-1}$)
 - two-cell: $85\text{-}95\text{ cm}^3/\text{min}$ ($1.4\text{e-}6$ - $1.6\text{e-}6\text{ m}^3\text{ s}^{-1}$)
- Oxygen flow rate: $400\text{-}600\text{ cm}^3/\text{min}$ ($1\text{e-}5$ - $6.6\text{e-}6\text{ m}^3\text{ s}^{-1}$)(STP)
- Pressure (reactor inlet/outlet): 700/500 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2 %
- Perforation diameter: 1.6 mm
- Constricted cathode

The comparison of modelled and experimental current efficiencies and specific energies of peroxide generation on medium single-cell reactor for polypropylene (SCIMAT 700/20) and for a micro-porous polyethylene-based diaphragm (SOLUPOR EH-06A) are shown in Figures 6.23 and 6.24.

Figure 6.23 Peroxide current efficiency versus superficial current density for medium single-cell reactor for modelled and experimental runs (other conditions as in section 6.2.6.6)

The results for the polyethylene-based diaphragm, as seen from the Figure 6.23, indicate that the current efficiency values are much higher than for the polypropylene-based diaphragm. The higher current efficiency values for polyethylene-based diaphragm are due to the lower convective losses through the polyethylene diaphragm (cf. Chapter 5, Appendix C). The current efficiency values for the polyethylene diaphragms were quite close to the modelled results for 2% perforations. This indicates a very good agreement between the model and the experimental results. The eddy diffusivity (D_{ed}) for modelling the two-cell reactor was kept as zero in a 2M NaOH solution indicating that there is very little convective peroxide loss through the polyethylene-based diaphragm.

Figure 6.24 Specific energy versus superficial current density for medium single-cell reactor for modelled and experimental runs (other conditions as in section 6.2.6.6)

Figure 6.25 Peroxide concentration versus superficial current density for medium single-cell reactor for modelled and experimental runs (other conditions as in section 6.2.6.6)

Also the experimental specific energies for peroxide generation for polyethylene-based diaphragm were much lower than that for polypropylene-based one as a result of the improved current efficiencies. However, the modelled specific energy values are still lower than experimental values on polyethylene diaphragms. A plausible reason for the lower specific energies predicted by the model compared to the measured values on polyethylene-based diaphragm may be because the oxygen generation on the anode was not included in the model. The generated oxygen causes an increased anode overpotential resulting in higher cell voltages and specific energies.

Figure 6.25 indicates that peroxide concentrations for the modelled results are close to the experimental values for polyethylene based diaphragm. The values differ slightly at current densities exceeding 3 kA m^{-2} due to the slightly different product flow rate ($6.6\text{e-}7 \text{ m}^3 \text{ s}^{-1}$ for modelled compared to $7.4\text{e-}7 \text{ m}^3 \text{ s}^{-1}$ for experimental results).

Figure 6.26 Peroxide current efficiency versus superficial current density for medium two-cell reactor for modelled and experimental runs (other conditions as in section 6.2.6.6)

Having selected a suitable diaphragm (SOLUPOR: EH-06A providing current efficiencies $> 80\%$ at current densities $> 3 \text{ kA m}^{-2}$ on a single-cell), experiments were done in the medium two-cell reactor using the same diaphragm. The current efficiency and specific energy for peroxide generation are compared in Figures 6.26 and 6.27 respectively.

Figure 6.27 Specific energy for peroxide generation versus superficial current density for medium two-cell reactor for modelled and experimental runs (other conditions as in section 6.2.6.6)

The results in Figures 6.26 and 6.27 for current efficiency and specific energy for generation on medium two-cell reactor are similar to that on the single-cell. The current efficiency for peroxide generation is much higher on the two-cell reactor employing the polyethylene-based diaphragm (SOLUPOR: EH-06A) compared to the polypropylene diaphragm (SCIMAT 700/20). The modelled peroxide current efficiencies are calculated for an eddy diffusivity (D_{ed}) of zero and are quite close to the experimental values for the polyethylene based diaphragm indicating that there is negligible peroxide loss due to convective flow through the diaphragm.

Also the specific energy values for peroxide generation in the two-cell reactor employing the polyethylene-based diaphragm are closer to the modelled values, indicating that scale-up has been achieved.

6.2.6.7 Comparison of model predictions with experimental results for a medium four-cell reactor

Experiments were also carried on four bipolar cells using the polyethylene-based diaphragm (SOLUPOR EH-06A). The current efficiency for peroxide generation based on experiments on four cell runs is compared with the modelled results in Figure 6.28.

The conditions for operating the four-cell reactor are given below:

- NaOH concentration: 2 M
- Diaphragm: SOLUPOR EH-06A
- NaOH flow rate: 185 cm³/min (3.1e-6 m³ s⁻¹)
- Oxygen flow rate: 1200 cm³/min (2e-5 m³ s⁻¹)(STP)
- Pressure (reactor inlet/outlet): 925/575 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2 %
- Perforation diameter: 1.6 mm
- Constricted cathode

The experimental peroxide current efficiencies were low compared to modelled values. The low current efficiencies in the four-cell runs are largely due to the maldistribution of gas and liquid between the cells in the perforated bipole electrochemical reactor. The maldistribution of gas and liquid occurs because of inappropriate flow channels in the reactor. At the bottom of each cell are provided flow channels to allow uniform liquid and gas flow in each cell. However due to variable compression on the reactor some of the flow channels at the bottom compress into the gasket causing gas and liquid maldistribution. Better flow channels for inter-cell

manifolding may be designed in future to improve the current efficiency in the perforated multi-cell electrochemical reactor for peroxide generation.

At 0.5 kA m^{-2} , peroxide current efficiency of about 83% was seen for the four-cell run in one of the experiments. Also in Figure 6.28 the peroxide current efficiency is 78% at 0.5 kA m^{-2} . Such high current efficiencies indicate that peroxide could be generated efficiently at low current densities, however these experiments are extremely difficult to replicate. Also the current bypass through the perforations decreases with increasing current density so that high current efficiencies ($> 75\%$) at current densities $> 2 \text{ kA m}^{-2}$ are theoretically possible for a four-cell reactor.

Figure 6.28 Peroxide current efficiency versus superficial current density for medium four-cell reactor for modelled and experimental runs (other conditions as in section 6.2.6.7)

6.3 Sensitivity of kinetic parameters for reaction (2.3) and (2.4)

The kinetic parameters for perhydroxyl, HO_2^- ion generation k_1^0 and reduction k_2^0 based on reaction (2.3) and (2.4) respectively are chosen from Sudoh et al. (1985a).

However, the kinetic parameters on graphite felt may differ from that given by Sudoh et al. (1985a). Therefore it is prudent to do an analysis to see the sensitivity of the kinetic parameters namely, k_1^0 and k_2^0 for reaction (2.3) and (2.4) on the peroxide current efficiency.

Figure 6.29 Sensitivity analysis of the kinetic parameters

The values of k_1^0 and k_2^0 were 5×10^{-7} and $1.6 \times 10^{-9} \text{ m s}^{-1}$ respectively. The small single-cell reactor was modelled on the four corner points of Figure 6.28 for peroxide current efficiency and results compared with the values at the centre ([Sudoh et al., 1985a]) in Figure 6.30. The eddy diffusivity (D_{ed}) in the model was chosen as $2 \times 10^{-8} \text{ m s}^{-1}$.

It may be seen from Figure 6.30 that the peroxide current efficiency differs by less than 4% for the kinetic parameters chosen in Figure 6.29. The experimental current efficiencies are close to the modelled values for current densities exceeding 2 kA m^{-2} . At current densities $< 2 \text{ kA m}^{-2}$, the eddy diffusivity (D_{ed}) may be lower (cf. Figure 6.11). The factors were varied by an order of magnitude indicating that the peroxide current efficiency is not very sensitive to these values at the conditions given here. Therefore the

kinetic data of Sudoh et al. (1985a) gives a good measure of the peroxide efficiencies in the perforated bipole electrochemical reactor.

Figure 6.30 Modelled peroxide current efficiency vs superficial current density for different kinetic parameters on small single-cell reactor compared to experimental values

6.4 Error analysis

An error analysis on the current density, peroxide current efficiency and the specific energy for peroxide generation on the small and medium reactor is given in Appendix G.

For the small reactor the uncertainties in the current density and current efficiency are respectively ± 6 and $\pm 8\%$, while at 5 kA m^{-2} , the voltage fluctuated from 2.85 to 3.15 V, for a variation of $\pm 5\%$ and consequent uncertainty in the specific energy of $\pm 13\%$. These values are reflected in the error bars of Figures 6.11, 12, 13, etc.

For the medium reactor the corresponding uncertainty values were: current density $\pm 4\%$, current efficiency $\pm 5\%$ and specific energy $\pm 10\%$. These values are contained in the error bars of Figures 6.21, 6.22 etc. and correspond approximately to the confidence intervals from replicate runs.

In Figures 6.1, 6.2 etc., only the mean values have been provided for current density, current efficiency and specific energy as these graphs compare different diaphragms and anodes. Error bars are not shown in those graphs as they would complicate the plots.

Additional variance in the peroxide current efficiency and specific energy may arise in two-cell reactor due to the maldistribution of fluids between the cells.

In essence, the significance of agreement between the modelled and experimental results must be tempered by consideration of:

- 1) The hypothetical "eddy diffusivity factor" that is adjusted in the model to match the experimental results.
- 2) Maldistribution of liquid and gas between cells that may affect the peroxide current efficiency and specific energy.
- 3) The various levels of experimental errors and compounded in the calculation of figures of merit from measurements on current, flow rate etc.

CHAPTER 7

Process Synthesis, Economics and Technological Comparison

7.1 Introduction

Alkaline peroxide, as has been discussed in Chapter 1, can be used for a number of pulp bleaching applications. Conventionally hydrogen peroxide generated from the thermochemical process (auto-oxidation of anthraquinols: Chapter 1) is transported to and stored in a pulp mill as a 30-50%_w solution and then diluted to desired concentrations. To save on transportation and storage costs of peroxide, it is desired to have an economic analysis of the process utilizing the perforated bipole electrochemical reactor on site at a pulp mill.

The economic analysis is done for a process utilizing dilute solutions of alkaline peroxide viz. 2-3%_w in 2 M NaOH (ca. 7.5%_w) solution. It is assumed that the mill uses 10 tonnes per day of H₂O₂ (100% basis). This capacity was chosen to match the capacity of a typical rate of peroxide utilization [Mathur and Dawe, 1999]. The cost of NaOH is not included in the economic analysis as NaOH has to be added for the pulp bleaching applications even if other bleaching agents viz. ClO₂, O₃, etc. are used in place of hydrogen peroxide.

7.2 Operational Conditions

The following operational conditions are used in the economic evaluation of the process utilizing a perforated bipole electrochemical reactor for the generation of alkaline peroxide:

Cell components:

Cathode: Graphite felt (Metaullics systems Inc)

Diaphragm:	Microporous-polyethylene (DSM Solutech, Holland)
Anode:	Nickel mesh (Argus Inc.) and Grafoil (Union Carbide)
Gaskets:	Durabla (Neoprene and asbestos based)
Superficial current density:	1000 - 5000 A m ⁻²
Peroxide current efficiency	
and cell voltage:	Based on the 20-cell large reactor (1800 mm by 250 mm))
Operation mode:	Bipolar, galvanostatic and single pass upward G/L flow
Inlet/outlet pressure:	1200/300 kPa (abs.)
Inlet temperature:	294 K
Peroxide generation rate:	10 TPD (100% basis) or 12.3 kmol h ⁻¹
Product flow rate:	(~ 2% _w H ₂ O ₂ solution) 21 m ³ h ⁻¹
O₂ requirement:	6.15 kmol h ⁻¹ (Vacuum swing adsorbed (VSA) O ₂)
O₂ flow rate (compressor):	7.7 kmol h ⁻¹ or 180 m ³ h ⁻¹ (STP) (1.25 stoichiometric)
NaOH feed:	2M (7.5% _w)

7.3 Gross economic potential (GEP)

The net stoichiometry for the peroxide generation reaction is:

The additives shown in Table 7.1 are combined with the feed (cf. Chapter 4) and their costs have to be accounted for in the GEP.

The gross economic potential associated with the production of 12.3 kmol h⁻¹ peroxide is given by:

$$\begin{aligned} \text{GEP} &= [\text{Value of products}] - [\text{Value of feeds}] - [\text{Value of additives}] \quad (7.2) \\ \text{GEP} &= 12.3 \times 34 \times 0.75 - 6.15 \times 32 \times 0.25 - 12.3 \times 18 \times 0.01 - 12.3 \times 18 \times 0.002 \times 0.01 \times 5 - \\ &\quad 12.3 \times 18 \times 0.1 \times 0.01 \times 10 = \$ 260 \text{ h}^{-1} \end{aligned}$$

The targeted price of 0.75 US \$ kg⁻¹ for H₂O₂ is the current market price of commercial peroxide based on the February 2003 data [manufacturing.net, 2003]

Table 7.1 Value of reagents & products US \$

Reagents and products	Cost	Source
Makon NF-12 (0.002 % _w)	\$ 5/kg	Stepan Chemical Co.
DTPA (0.1 % _w)	\$10/kg	Hart Chemicals
O ₂	\$ 0.25/kg	Air Liquide
H ₂ O ₂	\$ 0.75/kg	manufacturing.net
H ₂ O	\$ 0.01/kg	-
NaOH (bleaching reagent)	0	-
Electricity	\$ 0.03/kWh	[Mathur and Dawe,1999]

The gross economic potential is a first measure of the potential viability of the process. Any process with a negative GEP is not economically viable and therefore can usually be discarded from an economic standpoint. The process may only be considered if there is a strategic, military or political need for it.

In the present process a GEP of 260 US \$ h⁻¹ provides a sufficient reason for the process to be evaluated further.

7.4 Net economic potential (NEP) and return on investment (ROI)

The net economic potential provides a more realistic analysis of the process and the assessment is expanded to include the different types of equipment and the various flow streams. The capital and operational cost estimates can be obtained based on a preliminary design and sizing of the process equipment.

The net economic potential is derived from the following equation [Oloman, 1996]:

$$\text{NEP} = \text{GEP} - \text{Cost of (utilities + labour + maintenance)} \quad (7.3)$$

Options with a negative GEP can be eliminated from further consideration, while options with a positive NEP can be ranked in order of the return on investment (ROI) which is estimated by the following equation:

$$ROI = \frac{\text{Annual NEP}}{\text{Capital cost}} \quad (7.4)$$

$$ROI (\% \text{ per year}) = \frac{8000 \text{ NEP}}{\text{Total installed capital cost}}$$

The number of hours of operation per year is typically 8000.

A conceptual flowsheet of the present process is shown in Figure 7.1.

Figure 7.1 Flowsheet for alkaline peroxide electrosynthesis

The major cost in the system is that of the electrochemical reactor. The economic evaluation of the present process is based on the equipment shown in Figure 7.1.

The total installed capital cost of the electrochemical reactor unit $C_{I,E}$ is the sum of the installed capital cost of the cells C_{IEC} and the installed capital cost of the power supply system, C_{PS} . Or

$$C_{I,E} = C_{IEC} + C_{PS} \quad (7.5)$$

The installed capital cost for electrochemical reactors, C_{IEC} is given by [Oloman, 1996]:

$$C_{IEC} = N_c G_c (A_c)^{m'} \quad (7.6)$$

where N_c is the number of cells, G_c is the cost constant expressed in $\$ m^{-2}$, A_c is the electrode area per cell (m^2) and m' scale exponent (0.8-0.9). The cost estimate of the cell components is shown in Table 7.2 below:

Table 7.2 Cost estimate of cell components (F.O.B.)

Cell component	Cost estimate per US \$ m^{-2} superficial electrode area
Graphite felt cathode	50
Nickel mesh anode	400
Grafoil anode	300
Polyethylene diaphragm	50
Durabla gasket	100
End plates (averaged for 20 cells)	100
Miscellaneous	600
Total	\$1600

The total cost of cell components is US \$1600/ m^2 (Table 7.2) and the installed reactor cost is obtained by multiplying the total cost of the cell components (per m^2) by a

Lang factor of 3 [Janson, 1984]. For the present case the cost of the installed reactor is 4800 US \$ m⁻². Most of the reactor components usually have to be replaced every six months and therefore the cost component G_c is double the installed reactor cost and is 9600 US \$ m⁻² in the present work.

The cathode area and the number of required cells are related through Faraday's law i.e.

$$N_c = \frac{n_o F P_r}{i A_c (C.E.)} \quad (7.7)$$

where n_o is the number of electrons involved in the process (2), F is the Faraday's constant (96486 kC kmol⁻¹), P_r is the peroxide production rate (kmol s⁻¹), i is the superficial current density (kA m⁻²) and C.E. the current efficiency.

The superficial electrode area per cell is based on the design considerations of the cell. For the present case an area of 0.45 m²/cell is chosen based on the size of the large or commercial reactor, i.e. 1800 mm by 250 mm (Chapter 3).

The cost of the electrical energy (DC supply) associated with the electrochemical reactor, C_{el} (US \$ h⁻¹) is [Oloman, 1996]:

$$C_{el} = \frac{C_{ac} P_w}{RE} \quad (7.8)$$

where C_{ac} is the cost of ac electricity (0.03 US \$ kWh⁻¹) [Mathur and Dawe, 1999], RE is the rectifier efficiency (0.96) and where P_w is the total power consumption (kW) given by:

$$P_w = N_c A_c i V_c \quad (7.9)$$

$$V_r = N_c V_c \quad (7.10)$$

where V_r is total voltage of the reactor (V) and V_c the voltage per cell (V).

The installed capital cost of the power supply system is [Oloman, 1996]:

$$C_{PS} = P_w \left(B' + \frac{C'}{V_r} \right) \quad (7.11)$$

where B' and C' are the cost constants (100 and 20,000 \$ kW⁻¹). The cost of DC power supply for different current densities is listed in Table 7.3.

Table 7.3 Cost of DC power supply system

Superficial current density kA m ⁻²	Installed capital cost US \$
1.1	132858
2.4	167194
3.2	187948
3.9	214768
5.5	311454

The cost of the installed auxiliary equipment (Figure 7.1) viz. tank, pump, etc. is given in Table 7.4 and the calculations are shown in Appendix H. The cooling water cost is assumed to be 0.03 US \$ m⁻³.

Table 7.4 Cost of auxiliary equipment and utilities

Equipment	Uninstalled cost US \$	Installation factor	Installed capital cost (C _{IA}) US \$	Power kW	Cooling water m ³ h ⁻¹	Electrical energy/ cooling water US \$ h ⁻¹
Feed tank	14300	3	42900			
Storage tank	14300	3	42900			
Pump	10400	4.5	46800	6.5		0.2
Two-stage compressor	8400	4.5	37800	18.8		0.6
G/L separator	1700	4	6800			
Product cooler	39400	3	118200		105	3.2
Total	88500		295400			4

The total installed capital cost (C_{IC}) is therefore the sum of the installed capital cost of the electrochemical reactor (C_{IEC}), installed cost of power supply equipment (C_{PS}) and the installed capital cost of auxiliary equipment (C_{IA}). In other words:

$$C_{IC} = C_{IEC} + C_{PS} + C_I \quad (7.12)$$

The maintenance and labour costs ($C_{E,ML}$) associated with the electrochemical plant ($\$ \text{ year}^{-1}$) is typically 5-10% of the total capital cost [Oloman, 1996]. For the present study the maintenance cost is chosen as 10% of the total installed capital cost (C_{IC}). Therefore,

$$C_{E,ML} = 0.1 C_{IC} \quad (7.13)$$

The economic analysis is done for plant using a 20-cell reactor, producing a maximum of 0.80 M ($\sim 2.3\%_w$) alkaline peroxide in 2M ($7.5\%_w$) NaOH with a product flow rate of $6e-4 \text{ m}^3 \text{ s}^{-1}$ per cell. The plots of peroxide concentration, current efficiency and specific energy versus superficial current density for a large reactor with 2 and 20 cells are shown in Figures 7.2, 7.3 and 7.4 respectively.

The curves in Figures 7.2, 7.3 and 7.4 obtained from the two-cell model (cf. Chapter 5) indicate that the peroxide current efficiency and peroxide concentration decreases marginally for a 20-cell reactor in comparison with a 2-cell reactor, whereas the specific energy for peroxide generation increases marginally. The small difference in the peroxide concentration, peroxide current efficiency and specific energy for peroxide generation in a 2 and 20-cell reactor may be attributed to the assumption of uniform gas and liquid distribution in between the cells.

Figure 7.2 Peroxide concentration versus superficial current density in a 2 & 20-cell commercial reactor (1800mm by 250mm)

Figure 7.3 Peroxide current efficiency versus superficial current density in a 2 & 20-cell commercial reactor (1800mm by 250mm)

Figure 7.4 Specific energy for peroxide generation versus superficial current density in a 2 & 20-cell commercial reactor (1800mm by 250mm)

Figure 7.5 Product outlet temperature versus superficial current density in a commercial reactor (1800mm by 250mm)

Figure 7.5 also shows the product outlet temperature versus superficial current density for the modelled commercial reactor. It may be observed that the electrolyte temperature is 374 K at 4.8 kA m^{-2} and 390 K at 5.5 kA m^{-2} . Such high temperatures may cause material failure viz. polyethylene diaphragm and Grafoil anode and also lead to peroxide decomposition that has not been accounted for in the model. Therefore, cooling of the reactor is essential for the efficient operation of the perforated bipole electrochemical reactor.

Figure 7.6 shows that the highest NEP is at a superficial current density of 3.2 kA m^{-2} i.e. $\$ 210 \text{ h}^{-1}$ approx. On the other hand in Figure 7.9, the ROI peaks at 4.8 kA m^{-2} . The increase in ROI is largely due to the reduced number of cells (1840 at 1.1 kA m^{-2} i.e. 90 reactors with 20 cells per reactor to 441 at 5.5 kA m^{-2} i.e. 22 reactors with 20 cells per reactor) needed to produce 10 TPD hydrogen peroxide that lowers the installed capital cost from USD 9.9 million at 1 kA m^{-2} to USD 2.9 million at 5.5 kA m^{-2} (Figure 7.7).

Figure 7.6 Net economic potential versus superficial current density for peroxide generation

Figure 7.7 Installed capital cost versus superficial current density for peroxide generation

Figure 7.8 Operating cost versus superficial current density for peroxide generation

Figure 7.8 shows that the operating cost first decreases and then increases with increasing superficial current density. This trend in operating cost is due to the fact that to process 10 TPD of peroxide the number of reactors decreases causing a decrease in the labour and maintenance cost. Whereas the power consumption increases increasing the electricity cost.

Figure 7.9 Return on investment versus superficial current density for peroxide generation

Generally investment considerations are given to processes with $\text{ROI} > 30\%$ per year [Oloman, 1996]. In order to maximize profits (NEP) the process would be most suited to run at a superficial current density of 4.8 kA m^{-2} . However, other considerations such as Joule heating, anode longevity and increased capital cost due to cell replacement frequently may prevent the cell to be operated at such a high current density (4.8 kA m^{-2}).

The superficial current density in the present study based on maximizing NEP is around 3.2 kA m^{-2} (cf. Figure 7.6). Also, ROI at 3.2 kA m^{-2} is $> 30\%$ and therefore in the long term 3.2 kA m^{-2} is a more suitable current density than 4.8 kA m^{-2} .

In essence the choice of operating current densities rests on the practical achievability of current efficiencies to match the theoretical values in Figure 7.3, the stability of cell components (at temperatures > 353 K and current densities > 4 kA m⁻²), the net economic potential and the return on investment.

7.5 Technological comparison

Table 7.4 provides a comparison of the various technologies, in terms of the number of cells, peroxide current efficiency, voltage per cell etc., that are currently available for peroxide generation.

The data on the gas diffusion reactor is provided by Kvaerner-Chemetics, Vancouver, Canada who have developed a monopolar reactor with two cells for peroxide generation [Twardowski, unreported]. The reactor developed by Kvaerner-Chemetics successfully demonstrated for a continuous operation for over 12000 hours in a 187 e-4 m² reactor, 0.25 m high. The product strength was maintained at 5%_w during their test. The NaOH concentration was about 8%_w.

Table 7.4 Comparison of the UBC, Gas diffusion and the Dow-Huron reactor

Reactor type	Format	Reactor length, m	Cells per reactor	Current density, kA m ⁻²	Peroxide current efficiency, %	Voltage per cell, V	Operating Pressure, kPa abs. Inlet/Outlet	Operating Temp., K	NaOH conc., M
UBC (present)	bipolar	0.6	2	5	78	3	900/600	70+	2
UBC (proposed)	bipolar	1.8	20	5	65	3	900/600	70+	2
Dow-Huron	monopolar	1	2	0.6	85	2.4	110 inlet	40	2
Gas diffusion	monopolar	0.25	2	2	98	2.4	100 inlet	40	2

Table 7.4 shows the Dow-Huron and the gas diffusion reactor to be superior to the UBC reactor in terms of the peroxide current efficiency, the lower operating voltages and

temperatures, however, the capital cost of the UBC reactor would be at least 2-3 times lower than that of the other two reactors. For the electrolytic peroxide generation process to be competitive, the capital cost should be low so that a process on-site a pulp is economically viable.

However, a detailed economic study is needed for the Dow-Huron and the gas diffusion based reactor to make a better economic comparison.

The commercial UBC reactor will probably be limited to produce NaOH to H₂O₂ ratios greater than 2.5. A lower ratio than 2.5 would probably reduce the life of the reactor as the pH on the anode in such cases would decrease to levels that may corrode the anode more frequently. Lower caustic to peroxide ratios are needed in most pulp bleaching applications and therefore the present process may be limited to some specific kinds of bleaching applications that require caustic to peroxide ratios greater than 2.5.

CHAPTER 8

Conclusions and Recommendations for Future Work

8.1 Conclusions

The following conclusions can be drawn from the present Thesis work:

1. A novel method to model the perforated bipole electrochemical reactor has been developed. The reactor model has a novelty in terms of modelling the 3D electrode using an electronic analogue circuit previously unreported in literature (cf. Chapter 5 and Appendix E).
2. The perforated bipole electrochemical reactor has been scaled-up from small to medium size for one and two-cells (current efficiency $> 80\%$ at 3 kA m^{-2} , specific energy $< 8 \text{ kWh kg}^{-1}$ for peroxide generation). The maximum peroxide concentration achieved was 0.55 M ($\sim 1.5\%_{\text{w}}$) in 2M ($7.5\%_{\text{w}}$) NaOH solution. The scale-up was achieved due to a better gas and liquid distribution in a cell which was made possible by employing constricted cathodes. The improved cell performance is largely a result of the new diaphragm (SOLUPOR EH-06A). In four-cell runs high current efficiencies (as in one and two-cells) were not achieved, probably due to the maldistribution of gas and liquid between the cells.
3. Various electrode materials were tried to seek a good anode for use in the present work. It was found that nickel mesh (100) in conjunction with the perforated Grafoil served as a good anode material that was easily fabricable in the laboratory and could be used in future in other electrochemical systems where low overpotential for oxygen evolution is an issue.

4. A new bipolar anode has been invented that can lower the current bypass through the perforated bipole substantially (cf. Chapter 4 and 6). The bipole uses three perforated Grafoil sheets within which were inserted two PTFE sheets and polystyrene beads (cf. Figure 4.6). This novel bipolar electrode could be used in other industrial bipolar electrochemical reactors where gas generation at one of the electrodes is an issue.
5. A process economic model developed for 10 tonnes per day alkaline peroxide (100%w H_2O_2 basis) production indicates that peroxide generation is economically viable (i.e. return on investment > 30%) in a perforated bipole reactor at superficial current densities exceeding 2.0 kA m^{-2} .

8.2 Recommendations for future work

1. Peroxide current efficiency in a multi-cell (> 2) perforated bipole electrochemical reactor is dependent on the proper gas and liquid distribution between cells. The fluid distribution between cells should be studied to improve the performance of the multi-cell reactor. Tracer tests as shown in Figure 8.1 may be done to improve the performance of the perforated bipole multi-cell electrochemical reactor.

Figure 8.1 Tracer tests for flow distribution study

2. Investigate different cathode and diaphragm properties e.g. compression, thickness, porosity and their variation along the reactor length to optimize the reactor performance.
3. Study the performance of the large reactor for peroxide generation. Flow problems in a large single-cell may be an issue as the width of the large reactor is about six times that of the medium reactor. Therefore for a uniform gas and electrolyte flow the cathode may have to be cut in five different sections as shown Figure 8.2.

Figure 8.2 Large cell configuration

4. Convection factor (eddy diffusivity, D_{ed}) in the present modelling work has been guessed to make the modelled peroxide current efficiency fit the experimental values. In future experiments could be conducted using peroxide solutions containing reagents such as ferri/ferro cyanide on the small and the medium reactor to measure the eddy diffusivity. The aim of such experiments would be prevent peroxide generation or reduction on the cathode, at the same time letting peroxide oxidation occur on the anode. Knowing the overall peroxide loss, the convective loss may be accounted for by subtracting the diffusive and migrative losses on the anode.

Nomenclature

Symbol	Meaning	Units
A_c	Superficial electrode area per cell	m^2
A_{ex}	Heat transfer area for heat exchanger	m^2
a	Tafel parameter	V
a_a	Tafel parameter for reaction (2.11) on the anode	V
a_{c1}	Tafel parameter for reaction (2.3) on the cathode	V
a_{c2}	Tafel parameter for reaction (2.4) on the cathode	V
B'	Cost constant (\$100)	
b	Tafel parameter	V decade ⁻¹
b_a	Tafel slope for reaction (2.11) on the anode	V decade ⁻¹
b_{c1}	Tafel slope for reaction (2.3) on the anode	V decade ⁻¹
b_{c2}	Tafel slope for reaction (2.4) on the anode	V decade ⁻¹
C	Reactant concentration	$kmol\ m^{-3}$
C'	Cost constant (\$100/kW)	
C_{aOH^-}	Concentration of hydroxyl ion on the anode side	$kmol\ m^{-3}$
$C.B.$	Fraction current bypass in the reactor	dimensionless
$C.E.$	Current efficiency	dimensionless
C_{ac}	Unit cost of electrical energy	\$ kW ⁻¹
C_{el}	Cost of electrical energy	\$ h ⁻¹
$C_{electrolyte\ (j)}$	Concentration of electrolyte j (Appendix B)	$kmol\ m^{-3}$
$C_{electrolyte,\ O_2}$	O ₂ concentration in electrolyte (Appendix B)	$kmol\ m^{-3}$
$C_{E,ML}$	Labour and maintenance cost	\$ year ⁻¹
$C_{HO_2^-}$	Concentration of per hydroxyl ion	$kmol\ m^{-3}$
$C_{H_2O,\ O_2}$	O ₂ concentration in water(Appendix B)	$kmol\ m^{-3}$
C_{IA}	Installed capital cost of the auxiliary system	\$
C_{IC}	Total installed capital cost of the electrochemical system	\$
$C_{I,E}$	Installed capital cost of electrochemical reactor unit	\$
C_{IEC}	Installed capital cost of electrochemical cells	\$
C_{Na^+}	Concentration of sodium ion	$kmol\ m^{-3}$
C_{Ob}	Bulk concentration of oxidized species	$kmol\ m^{-3}$
C_{Os}	Concentration of oxidized species at electrode surface	$kmol\ m^{-3}$
C_{Rb}	Bulk concentration of reduced species	$kmol\ m^{-3}$
C_{Rs}	Concentration of reduced species at electrode surface	$kmol\ m^{-3}$
C_{O_2}	Concentration of oxygen	$kmol\ m^{-3}$
C_{OH^-}	Concentration of hydroxyl ion	$kmol\ m^{-3}$
C_p	Specific heat for O ₂ at constant pressure	J mol ⁻¹ K ⁻¹
C_{PS}	Installed capital cost of power supply system	\$
C_r	Number of centre point runs	dimensionless
C_v	Specific heat for O ₂ at constant volume	J mol ⁻¹ K ⁻¹
c_l	Liquid heat capacity	kJ kg ⁻¹ K ⁻¹

c_g	Gas heat capacity	$\text{kJ kg}^{-1}\text{K}^{-1}$
D	Dispersion coefficient	m^2s^{-1}
$D_{\text{HO}_2^-}$	Diffusivity of perhydroxyl ion	m^2s^{-1}
D_{diff}	Diffusion coefficient	m^2s^{-1}
D_{O_2}	Diffusivity of oxygen	m^2s^{-1}
D_{OH^-}	Diffusivity of perhydroxyl ion	m^2s^{-1}
D_{Na^+}	Diffusivity of sodium ion	m^2s^{-1}
$D_{\text{HO}_2^-}^0$	Diffusivity of perhydroxyl ion at infinite dilution	m^2s^{-1}
$D_{\text{O}_2}^0$	Diffusivity of oxygen at infinite dilution	m^2s^{-1}
$D_{\text{OH}^-}^0$	Diffusivity of hydroxyl ion at infinite dilution	m^2s^{-1}
$D_{\text{Na}^+}^0$	Diffusivity of sodium ion at infinite dilution	m^2s^{-1}
$D_{\text{dHO}_2^-}$	Effective diffusivity of perhydroxyl ion in the diaphragm	m^2s^{-1}
D_{dOH^-}	Effective diffusivity of hydroxyl ion in the diaphragm	m^2s^{-1}
D_{ed}	Eddy diffusivity of hydroxyl ion (convection)	m^2s^{-1}
D_L	Diffusivity of liquid	m^2s^{-1}
D_{sep}	Diameter of gas-liquid separator	m
d_e	Equivalent diameter of the cathode bed	m
d_f	Fibre diameter	m
E_a	Activation energy in (A-20)	J mol^{-1}
E_{a1}	Activation energy for reaction (2.3) on carbon	J mol^{-1}
E_{a2}	Activation energy for reaction (2.4) on carbon	J mol^{-1}
$E_{\text{H}_2\text{O}_2}$	Activation energy for H_2O_2 decomposition reaction (2.9)	J mol^{-1}
F	Faraday's constant (96486)	kC kmol^{-1}
F_v	Volumetric flow rate of electrolyte feed	m^3s^{-1}
F_{vgas}	Volumetric flow rate of gas (O_2)	m^3s^{-1}
$F_{\text{v,c}}$	Volumetric flow rate of cooling water	m^3s^{-1}
f_d	Degrees of freedom	dimensionless
G	Gas load	$\text{kg m}^{-2}\text{sec}^{-1}$
Ga_L	Modified Galileo number	dimensionless
GEP	Gross economic potential	$\text{\$ h}^{-1}$
G_c	Cost constant	$\text{\$ m}^{-2}$
g	Gas (oxygen) flow rate	kg s^{-1}
g_a	Acceleration due gravity (9.8)	m s^{-2}
H	Henry's constant for oxygen in NaOH	$\text{kmol kg}^{-1}\text{m}^{-2}\text{sec}^2$
H_o	Henry's constant for oxygen in H_2O	$\text{kmol kg}^{-1}\text{m}^{-2}\text{sec}^2$
h_G	Sechenov parameter (Appendix B)	dimensionless
h_i	Sechenov parameter (Appendix B)	dimensionless
h_l	Liquid hold up	dimensionless
I_{reactor}	Total current fed to the reactor	Amperes
I_1	Current (Appendix D)	Amperes
I_2	Current (Appendix D)	Amperes
I_3	Current (Appendix D)	Amperes
i	Total superficial current density on the anode	kA m^{-2}
i_b	Current density in electrolyte phase	kA m^{-2}

$i_{\text{HO2-}}$	Superficial current density for reaction (2.10) on the anode	kA m^{-2}
$i_{\text{OH-}}$	Superficial current density for reaction (2.11) on the anode	kA m^{-2}
i_s	Current density in electrode phase	kA m^{-2}
i'	Current density	A m^{-2}
j	Current density	kA m^{-2}
j_a	Current density for anodic reaction	kA m^{-2}
j_c	Current density for cathodic reaction	kA m^{-2}
j_{cathode}	Total real current density for reaction (2.3) & (2.4) on the cathode	kA m^{-2}
$j_{\text{HO2-}}$	Real current density for reaction (2.3) on the graphite felt cathode	kA m^{-2}
$j_{\text{OH-}}$	Real current density for reaction (2.4) on the graphite felt cathode	kA m^{-2}
j	current density	kA m^{-2}
j_i	Current density for reaction i in Appendix A	kA m^{-2}
j_L	Mass real transfer limited current density for oxygen transfer	kA m^{-2}
$j_{L,s}$	Mass transfer superficial limited current density for oxygen transfer	kA m^{-2}
j_{lim1}	Mass transfer limited real current density for oxygen transfer	A m^{-2}
j_{lim2}	Mass transfer limited real current density for perhydroxyl ion transfer	A m^{-2}
$j(1)$	Total superficial current density on the anode for (2.10) & (2.11)	A m^{-2}
$j(k)$	Real current density for (2.3) on cell1: where $k = 2, 4, \dots, (n-1)/2$	A m^{-2}
	Real current density for (2.4) on cell1: where $k = 3, 5, \dots, (n-1)/2 + 1$	A m^{-2}
	Real current density for (2.3) on cell 2: where $k = (n-1)/2 + 2, (n-1)/2 + 2 \dots (n-1)$	A m^{-2}
	Real current density for (2.4) on cell 2: where $k = (n-1)/2 + 3, (n-1)/2 + 5 \dots n$	A m^{-2}
	$n = 4m+1$, where m is an integer	
$j_{1\text{HO2-}}$	Real current density for reaction (2.3) on the graphite felt of cell 1	kA m^{-2}
$j_{2\text{HO2-}}$	Real current density for reaction (2.3) on the graphite felt of cell 2	kA m^{-2}
$j_{1\text{OH-}}$	Real current density for reaction (2.4) on the graphite felt of cell 1	kA m^{-2}
$j_{2\text{OH-}}$	Real current density for reaction (2.4) on the graphite felt of cell 2	kA m^{-2}
j_o	exchange current density for an electrochemical reaction	kA m^{-2}

j_{01}	exchange current density for reaction (2.3) on graphite	$A\ m^{-2}$
j_{02}	exchange current density for reaction (2.4) on graphite	$A\ m^{-2}$
j_{0a}	exchange current density for reaction (2.11) on nickel	$A\ m^{-2}$
k	Electrochemical rate constant in Appendix A	$m\ s^{-1}$
k_a	Electrochemical rate constant (anodic reaction) in Appendix A	$m\ s^{-1}$
$K_{s,j}$	Sechenov constant (Appendix B)	$l\ mol^{-1}$
$k_{acontact}$	Contact conductivity of grafoil and graphite felt	$S\ m^{-1}$
k_{apl}	Electrolyte (solution) conductivity	$S\ m^{-1}$
k_{apb}	Effective electrolyte conductivity in the graphite felt	$S\ m^{-1}$
k_{apd}	Effective electrolyte conductivity in the diaphragm	$S\ m^{-1}$
k_{aps}	Effective electrode conductivity (graphite felt)	$S\ m^{-1}$
k_c	Electrochemical rate constant (cathodic reaction) in Appendix A	$m\ s^{-1}$
$k_{grafail}$	Conductivity of grafoil	$S\ m^{-1}$
k_{perf}	Perforation electrolyte conductivity	$S\ m^{-1}$
k_g	Mass transfer coefficient for oxygen transfer in the gas phase	$m\ s^{-1}$
k_{H_2O}	Mass transfer coefficient for water transfer	$m\ s^{-1}$
$k_{HO_2^-}$	Overall mass transfer coefficient for per hydroxyl ion	$m\ s^{-1}$
k_{in}	Intrinsic rate constant for a reaction (Arrhenius type)	$m\ s^{-1}$
k_l	Mass transfer coeff. for O_2 transfer in liquid film at G-L interface	$m\ s^{-1}$
k_m	Mass transfer coefficient	$m\ s^{-1}$
k_O	Overall mass transfer coefficient for O_2 transfer	$m\ s^{-1}$
k_s	Mass transfer coeff. for O_2 transfer in liquid film at L-S interface	$m\ s^{-1}$
k_1	Electrochemical rate constant for reaction (2.3)	$m\ s^{-1}$
k_2	Electrochemical rate constant for reaction (2.4)	$m\ s^{-1}$
k^0	Electrochemical rate constant at a defined temperature	$m\ s^{-1}$
k_1^0	Electrochemical rate constant for reaction (2.3) at 288 K	$m\ s^{-1}$
k_2^0	Electrochemical rate constant for reaction (2.4) at 288 K	$m\ s^{-1}$
k_a^0	Standard rate constant (anodic)	$m\ s^{-1}$
k_c^0	Standard rate constant (cathodic)	$m\ s^{-1}$
L'	Characteristic length	m
LMTD	Log mean temperature difference	K
l_e	Length of reactor	m
lin	Number of length increments of the reactor	dimensionless
liq	Liquid flow rate (electrolyte)	$kg\ s^{-1}$
ln	Log to the base e (2.7123 approx.)	
log	Log to the base 10	
M_{O_2}	Molecular weight of oxygen (0.032)	$kg\ mol^{-1}$
$MW_{product}$	Molecular weight of product	$kg\ kmol^{-1}$
m_v	Molar flow rate of oxygen	$mol\ s^{-1}$
m'	scale exponent (0.8-0.9)	
m_l	Order of electrochemical reaction (Appendix A)	

m ₂	Order of electrochemical reaction (Appendix A)	
N	flux of species across a plane perpendicular to x direction in equation (A-28)	kmol m ⁻² s ⁻¹
N _C	Number of electrochemical cells for producing 10 tonnes/day peroxide	
N _r	Number of factorial runs	dimensionless
NEP	Net economic potential	\$ h ⁻¹
NHE	Normal hydrogen electrode potential (298 K and 101 kPa abs.): defined as 0 V	V
n	Number of equations to be solved for the two cell reactor where n = 4m+1, where m is an integer	
n _{cell}	Number of cells in the reactor	
n _i	Number of ions in the electrolyte (Appendix B)	dimensionless
n _o	Number of electrons exchanged in the reaction	dimensionless
perf	Fraction perforation area in the bipolar electrode	dimensionless
P	Reactor pressure	kPa
P _{H₂O}	Vapour pressure of water	kPa
P _{in}	Compressor inlet pressure	kPa
P _{O₂}	Partial pressure of O ₂	kPa
P _{out}	Compressor outlet pressure	kPa
P _r	Peroxide production rate	kmol s ⁻¹
P _w	Total power consumption	kW
Q	Heat transferred	J s ⁻¹
R	Gas constant, (8.314)	J mol ⁻¹ K ⁻¹
RE	Rectifier efficiency	dimensionless
ROI	Return on investment	dimensionless
Re _G	Gas Reynold's no	dimensionless
Re _L	Liquid Reynold's no	dimensionless
R ₁	Resistance (Appendix D)	Ohm
R ₂	Resistance (Appendix D)	Ohm
R ₃	Resistance (Appendix D)	Ohm
Sc _L	Liquid Schmidt no	dimensionless
S.E.	Specific energy (electrochemical)	kWh kg ⁻¹
s	Specific surface area of the bed	m ⁻¹
s _t	Response error estimate	dimensionless
T	Temperature	K
T _{in}	Inlet temperature to the compressor	K
T _{c,in}	Process stream inlet temperature to heat exchanger	K
T _{c,out}	Process stream outlet temperature to heat exchanger	K
T _{p,in}	Process stream inlet temperature to heat exchanger	K
T _{p,out}	Process stream outlet temperature to heat exchanger	K
t _b	Cathode matrix (graphite felt) thickness after compression	m
t _d	Diaphragm thickness	m

t_o	Cathode matrix (graphite felt) thickness before compression	m
t_{perf}	Thickness of perforation	m
t_s	student's statistic at the desired confidence level	dimensionless
u	Electrolyte velocity in direction of flux	m s^{-1}
U	Overall heat transfer coefficient for alkaline peroxide to water	$\text{W m}^{-2} \text{K}^{-1}$
U_G	Superficial gas velocity	m s^{-1}
U_L	Superficial liquid velocity	m s^{-1}
V_c	Voltage per cell	V
V_{cf}	Electrolyte potential at the face of the cathode bed	V
V_{contact1}	Contact resistance between grafoil and graphite felt at bipolar electrode	V
V_{contact2}	Contact resistance between grafoil and graphite felt at end cathode	V
V_d	Diaphragm potential drop	V
V_r	Reactor voltage	V
V_{ra}	Equilibrium potential for reaction (2.11) on anode	V
V_c^R	Equilibrium potential (measured w.r.t. SHE) of cathode	V
V_c^o	Standard equilibrium potential (measured w.r.t. SHE) of cathode at unit activity of reactants and products	V
V_{rc}	Equilibrium potential for a cathodic reaction	V
V_{rc1}	Equilibrium potential for reaction (2.3)	V
V_{rc2}	Equilibrium potential for reaction (2.4)	V
V_1	Voltage (Appendix D)	V
V_2	Voltage (Appendix D)	V
V_3	Voltage (Appendix D)	V
V'	Electrode potential	V
w	Width of the reactor	m
W_a	Wagner number (ratio of Faradaic to Ohmic current)	dimensionless
x	Distance	m
z	Number of electrons transferred in the rate controlling single charge transfer reaction (Appendix A)	dimensionless
$z_{\text{HO}_2^-}$	Charge on perhydroxyl ion (1)	dimensionless
z_{Na^+}	Charge on sodium ion (1)	dimensionless
z_{OH^-}	Charge on hydroxyl ion (1)	dimensionless

Greek Symbols	Meaning	Units
α	Charge transfer coefficient	dimensionless
α_1	Electrochemical charge transfer coefficient for reaction (2.3)	dimensionless
α_2	Electrochemical charge transfer coefficient for reaction (2.4)	dimensionless
γ	Ratio of specific heats (C_p/C_v)	dimensionless

ε_b	Graphite felt porosity after compression, dimensionless	
ε_c	Compressor efficiency	dimensionless
ε_d	Diaphragm porosity	dimensionless
ε_o	Graphite felt porosity at zero compression, dimensionless	
ε_p	Pump efficiency	dimensionless
η	Overpotential or driving force for an electrochemical reaction	V
η_a	Anodic overpotential	V
η_{aOH^-}	Overpotential for reaction (2.11) on anode	V
η_c	Cathodic overpotential	V
η_{c1}	Overpotential for reaction (2.3) on the cathode	V
η_{c2}	Overpotential for reaction (2.4) on the cathode	V
μ_G	Gas viscosity	$\text{kg m}^{-1} \text{sec}^{-1}$
μ_L	Liquid viscosity	$\text{kg m}^{-1} \text{sec}^{-1}$
v_{gas}	Gas velocity through gas-liquid separator	m s^{-1}
σ	Standard deviation	
τ	Residence time in the reactor	sec
τ_{max}	Maximum electroactive bed thickness	m
ρ_L	Liquid (electrolyte) density	kg m^{-3}
ρ_G	Gas (oxygen) density	kg m^{-3}
ϕ	potential	V
ϕ_s	Electrode potential	V
ϕ_b	Electrolyte potential	V
∇P_G	Gas pressure gradient	$\text{kg m}^{-2} \text{sec}^{-2}$
∇P_L	Liquid pressure gradient	$\text{kg m}^{-2} \text{sec}^{-2}$
∇P_{LG}	Two-phase pressure gradient	$\text{kg m}^{-2} \text{sec}^{-2}$
Δl	Length of the graphite felt fibre,	m
ΔH_{evap}	Heat of vaporization of water (42.85)	kJ mol^{-1}
ΔP_{diff}	Pressure differential at the inlet and outlet of pump	N m^{-2}
ΔP_{LG}	Two-phase pressure drop	$\text{kg m}^{-1} \text{sec}^{-2}$ or Pa
Δz	Thickness of the cross-section in Figure 5.8, m	
$\Delta \eta$	Overpotential difference across the cathode matrix	V

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APPENDIX A

Electrochemical reactions

A1. Kinetics of electrochemical reactions

A redox reaction equilibrium in general is given by equation (A-1), where O is the oxidized species and R is the reduced species.

Reaction (A-1) is the rate controlling single charge transfer reaction and z is the number of electrons transferred in the reaction [Pickett, 1979].

The reaction equilibrium may be disturbed by altering the electrode potential. Polarizing cathodically makes the reaction proceed in the left to right. Anodic polarization on the other hand reverses this process. At equilibrium the rates are equal therefore no net current flows.

The current which flows when the electrode is polarized cathodically represents the difference between the rates of the forward (cathodic) and reverse (anodic) reactions.

The current density, j , (kA m^{-2}) is considered +ve and is given by:

$$j = j_a - j_c \quad (A-2)$$

where j_c is the partial current density for the cathodic reaction and j_a that for the anodic reaction. By analogy with the chemical kinetics and by Faraday's law the rate of forward reaction for a first order reaction can be written as:

$$\frac{j_c}{zF} = k_c C_{O_s} \quad (A-3)$$

where k_c is the rate constant and C_{O_s} is the concentration of O at that point close to the electrode surface where O is discharged.

Appendix A

In an analogous way the rate of reverse reaction is given by:

$$\frac{j_a}{zF} = k_a C_{Rs} \quad (\text{A-4})$$

where k_a and C_{Rs} have corresponding meanings to those above.

Consequently equation (A-3) and (A-4) may be substituted into (A-2) that gives:

$$j = zFk_a C_{Rs} - zFk_c C_{Os} \quad (\text{A-5})$$

and k_c and k_a can be further expressed in terms of Arrhenius type rate constant (activation energy relationship) for a reaction in which the working electrode is a cathode:

$$k_c = k_c^0 \exp\left(\frac{\alpha zF V_c}{RT}\right) \quad (\text{A-6})$$

$$k_a = k_a^0 \exp\left(-\frac{(1-\alpha)zF V_c}{RT}\right) \quad (\text{A-7})$$

where k_c^0 and k_a^0 are standard rate constants referred to some particular electrode potential. Equations (A-6) and (A-7) imply that a fraction, $\alpha(V_c)$ of the cathode potential is effective in promoting the cathodic process, the remainder $(1-\alpha)(V_c)$ in promoting the reverse (anodic) process. The potential V_c is measured relative to SHE (Standard hydrogen electrode potential: H_2 at 101 kPa and 25 °C on a Pt electrode). The charge transfer coefficient α is a dimensionless quantity and is defined as the fraction of V_c that is effective in promoting the cathodic reaction.

The equilibrium potential is found from the Nernst equation [Oloman, 1996]:

$$V_c^R = V_c^0 + \left(\frac{RT}{zF}\right) \ln\left(\frac{C_{Ob}}{C_{Rb}}\right) \quad (\text{A-8})$$

where C_{Ob} and C_{Rb} are the bulk concentration of O and R. In equation (A-8) the concentration terms C_{Ob} and C_{Rb} are present instead activities for O and R respectively. The activity coefficients for O and R are assumed to be one and therefore the activities are replaced with concentrations.

The rate constants k_c and k_a in equation (A-5) may be eliminated by substituting from equation (A-6) and (A-7) to give:

Appendix A

$$j = z k_c^o \exp\left(\frac{\alpha z F V_c}{RT}\right) C_{Rs} - z k_a^o \exp\left(-\frac{(1-\alpha) z F V_c}{RT}\right) C_{Os} \quad (A-9)$$

At equilibrium $V_c = V_c^R$, and $j = 0$, $C_{Os} = C_{Ob}$ and $C_{Rs} = C_{Rb}$ therefore:

$$z k_c^o \exp\left(\frac{\alpha z F V_c^R}{RT}\right) C_{Rb} - z k_a^o \exp\left(-\frac{(1-\alpha) z F V_c^R}{RT}\right) C_{Ob} = j_o \quad (A-10)$$

Overpotential η is defined as the driving force of the electrochemical reaction and is given by:

$$\eta = V_c - V_c^R \quad (A-11)$$

Equation (A-9) may be manipulated into general form to give:

$$j = j_o \left[\exp\left(\frac{\alpha z F \eta}{RT}\right) \left(\frac{C_{Rs}}{C_{Rb}}\right) - \exp\left(-\frac{(1-\alpha) z F \eta}{RT}\right) \left(\frac{C_{Os}}{C_{Ob}}\right) \right] \quad (A-12)$$

Equation (A-12) is known as the Butler-Volmer equation.

For slow electrochemical reactions or fast electrochemical reactions occurring at low current densities, $C_{Os} = C_{Ob}$ and $C_{Rs} = C_{Rb}$ so that equation (A-12) may be modified to give:

$$j = j_o \left[\exp\left(\frac{\alpha z F \eta}{RT}\right) - \exp\left(-\frac{(1-\alpha) z F \eta}{RT}\right) \right] \quad (A-13)$$

If $|\eta| > 100$ mV (i.e. $\eta < -100$ mV for appreciable cathodic polarization) the reverse anodic reaction is negligible compared to the forward cathodic reaction, therefore:

$$j = -j_o \exp\left(-\frac{(1-\alpha) z F \eta}{RT}\right) \quad (A-14)$$

Appendix A

$$\eta = \left(\frac{RT}{(1-\alpha)zF} \right) \ln(j_o) - \left(\frac{RT}{(1-\alpha)zF} \right) \ln(|j|) \quad (\text{A-14a})$$

$$\eta = a + b \log(|j|) \quad (\text{A-14b})$$

where a is the Tafel intercept and b is the Tafel slope and equation (A-14,a,b) are termed the Tafel equation and are given by (A-14c,d):

$$a = \left(\frac{RT}{(1-\alpha)zF} \right) \ln(j_o) \quad (\text{A-14c})$$

$$b = -2.303 \left(\frac{RT}{(1-\alpha)zF} \right) \quad (\text{A-14d})$$

Using equation (A-12) η may be defined in a more general form as:

$$\eta = \left(\frac{RT}{(1-\alpha)zF} \right) \ln(j_o) - \left(\frac{RT}{(1-\alpha)zF} \right) \ln(|j|) - \left(\frac{RT}{(1-\alpha)zF} \right) \ln \left(\frac{C_{Ob}}{C_{Os}} \right) \quad (\text{A-15})$$

The first two terms in the equation (A-15) are the activation over-potential term for an electrochemical reaction. The third term is the "concentration over-potential". Equation (A-15) may further be simplified into:

$$a + b \log(|j|) - b \log \left(1 - \frac{|j|}{j_L} \right) \quad (\text{A-16})$$

where $j_L = zFk_m C_{Ob}$, that is the mass transfer limited current density.

The complete electrochemical reaction characteristics is shown by Figure A.1

- A-B kinetic control
- B-C mixed control (mass transfer and kinetic control)
- C-D mass transfer control
- D-E secondary reaction

Figure A.1 Current density vs electrode potential characteristics

A2. Effect of temperature on kinetics of electrochemical reactions

Electrochemical reaction in equation (A-9) may be defined by:

$$j = z k_c^o \exp\left(\frac{\alpha z F V_c}{RT}\right) C_{Rs}^{m_1} - z k_a^o \exp\left(-\frac{(1-\alpha) z F V_c}{RT}\right) C_{Os}^{m_2} \quad (A-17)$$

where m_1 and m_2 reaction orders for reduction and oxidation reactions respectively.

As in (A-10), j_o may be alternatively defined as:

$$j_o = z k_c^o \exp\left(\frac{\alpha z F V_c^R}{RT}\right) C_{Rb}^{m_1} \quad (A-18)$$

or as:

$$j_o = z F k_{in} \exp\left(\frac{-E_a}{RT}\right) \exp\left(\frac{\alpha z F V_c^R}{RT}\right) C_{Rb}^{m1} \quad (A-19)$$

and k_c^o is given by:

$$k_c^o = k_{in} \exp\left(\frac{-E_a}{RT}\right) \quad (A-20)$$

where k_{in} is the intrinsic cathode reaction rate constant and E_a the activation energy. The intrinsic rate constant is dependent on the electrode material and to some extent as electrolyte (double-layer) composition.

The exchange current density in an electrochemical reaction provides a measure of the rate at which the electrochemical reaction occurs.

In essence the rate of reaction in an electrochemical reaction as given in (A-19) is dependent on two Arrhenius type rate constants related to temperature and electrode potential. The rate of reaction is also dependent on the concentration C_{Ob} of the reactant to the power of $m1$ (the order of the anode reaction).

A3. Partial current densities, current efficiency and specific energy

If more than one electrochemical reaction is occurring on an electrode then the current density due to each reaction $j_1, j_2, \dots, j_n$, (kA m^{-2}) are referred to as partial current densities for that individual reaction. The total current density j_{total} , (kA m^{-2}) is given by:

$$j_{total} = \sum j_i \quad \text{for } i = 1, 2, \dots, n \quad (A-21)$$

The current efficiency (C.E.) for reaction i at the working electrode is given by:

$$\text{C.E.} = \frac{j_i}{j_{total}} \quad (A-22)$$

The current efficiency in a complete bipolar electrochemical reactor for a particular product is given by:

$$C.E. = \frac{n_o F (\text{product rate})}{n_{\text{cell}} I_{\text{reactor}}} \quad (A-23)$$

where I_{reactor} is the total current fed to the reactor, Amperes and n_{cell} is the number of cells in the reactor and product rate in mol s^{-1} .

Current efficiency defined in (A-22) may differ from that in (A-23) as the former does not account for the product loss due to the secondary reactions occurring at the working electrode, loss reaction at the counter electrode and/or in the bulk electrolyte.

The specific energy for product generation (kWh kg^{-1} product) is given by:

$$S.E. = \frac{n_o F |V_{\text{cell}}|}{n_{\text{cell}} MW_{\text{product}} C.E.} \quad (A-24)$$

where n_o is the number of electrons taking part in the reaction to produce the given product, V_{cell} is the cell voltage MW_{product} is the molecular weight of the product in kg kmol^{-1} .

A4. Current efficiency and specific energy for peroxide generation in the present work

The current efficiency for peroxide generation is based on equation (A-23) and is given by:

$$C.E. = \frac{2000F C_{\text{HO}_2} (\text{liq}/\rho_L)}{n_{\text{cell}} I_{\text{reactor}}} \quad (A-25)$$

where liq is the electrolyte flow rate, kg s^{-1} , ρ_L is the electrolyte density, kg m^{-3} , I_{reactor} is the total current fed to the reactor, Amperes and n_{cell} is the number of cells in the bipolar reactor.

The specific energy for peroxide generation ($\text{kWh kg}^{-1} \text{H}_2\text{O}_2$) is given by:

$$S.E. = \frac{2F|V_r|}{n_{\text{cell}} (3600)(34) C.E.} \quad (A-26)$$

where V_r is the reactor voltage, V and n_{cell} is the number of cells in the reactor.

A5. Full cell voltage balance

The full cell voltage balance for a planar cathode and anode separated by a separator is given by:

$$V_{\text{cell}} = V_c^R - V_c^R - \eta_c - \eta_a - V_{\text{ohm}} \quad (\text{A-27})$$

where η_c and η_a are the overpotentials at the cathode and anode respectively and V_{ohm} is the ohmic voltage drop in the separator, anolyte and catholyte.

The voltage balance given in equation (A-27) is applicable for planar electrodes only. For 3D electrodes a more complicated equation defines the voltage balance that is discussed in Appendix C.

A6. General flux equation

Material transport in electrochemical reactors is described by a set of algebraic and non-linear partial differential equations. The central equation of this set is the general flux equation (for one dimension) is given by [Oloman, 1996]

$$N = -D_{\text{iff}} \left(\frac{dC}{dx} \right) - D_{\text{iff}} \left(\frac{CzF}{RT} \right) + Cu \quad (\text{A-28})$$

where N is the flux of the species perpendicular to x direction, $\text{kmol m}^{-2} \text{s}^{-1}$, D_{iff} is the diffusion coefficient, $\text{m}^2 \text{s}^{-1}$, u is the electrolyte velocity in the direction of flux, m s^{-1} and ϕ is the potential, V .

The term on the right of (A-28) are the diffusion, migration and the convection terms respectively. Equation (A-28) is strictly applicable to dilute solutions (i.e. $< 0.01 \text{ M}$). The version of flux equation in concentrated solutions is extremely difficult to use, therefore equation (A-28) is commonly used and is also used in modelling of the peroxide reactor.

APPENDIX B

Oxygen solubility and electrolyte conductivity in sodium hydroxide solutions

B1. Calculation of oxygen solubility in electrolyte solutions

The oxygen solubility in an electrolyte solution viz. NaOH (1 and 2 M) may be calculated from improved Sechenov equation [Hermann et al, 1995]

$$\log \left(\frac{C_{\text{electrolyte, O}_2}}{C_{\text{H}_2\text{O, O}_2}} \right) = \sum_j K_{s,j} C_{\text{electrolyte } (j)} \quad (\text{B-1})$$

$$K_s = \sum_i (h_i + h_G) n_i \quad (\text{B-2})$$

where $C_{\text{electrolyte, O}_2}$ and $C_{\text{H}_2\text{O, O}_2}$ are the oxygen concentrations (at the same temperature and pressure) in electrolyte and pure water respectively, $K_{s,j}$ is the Sechenov constant for electrolyte j (l mol^{-1}) ($j=1$ for a single electrolyte), $C_{\text{electrolyte } (j)}$ is the concentration of electrolyte j (kmol m^{-3}), h_i is the parameter for ion i , (e.g. Na^+ : 0.1079, OH^- : 0.0918, H^+ :0), h_G is the parameter for gas (O_2 :0), n_i is the stoichiometry of ions in the electrolyte.

The Henry's constant for oxygen in equilibrium with NaOH may be defined by the following relation:

$$H = \frac{H_{\text{O}}}{(C_{\text{NaOH, O}_2} / C_{\text{H}_2\text{O, O}_2})} \quad (\text{B-3})$$

where H_{O} is the Henry's constant for oxygen in water and is given by Troman's equation [Tromans, 1998]

$$H_{\text{O}} = \exp \left[\frac{0.046T^2 + 203.35T \ln \left(\frac{T}{298} \right) - (299.378 + 0.092T)(T-298) - 20.591e3}{8.3144T} \right] \quad (\text{B-4})$$

Appendix B

Solubility of oxygen in NaOH and water at 293 K and 100, 900 kPa abs. is given in Table B-1 and a surface plot for oxygen solubility in water, 1M NaOH and 2M NaOH at different temperatures and pressures in Figures B.1-B.3.

Table B.1 Oxygen solubility in NaOH and water

Liquid	Pressure (kPa) abs.	Temperature (K)	O ₂ concentration (mM)
H ₂ O	100	293	1.38
H ₂ O	900	293	12.42
H ₂ O	900	353	7.13
NaOH (1M)	100	293	0.87
NaOH (1M)	900	293	7.84
NaOH (1M)	900	353	4.50
NaOH (2M)	100	293	0.55
NaOH (2M)	900	293	4.95
NaOH (2M)	900	353	2.84

Figure B.1 Oxygen solubility in water at different temperatures and pressures

Figure B.2 Oxygen solubility in 1 M NaOH at different temperatures and pressures

Figure B.3 Oxygen solubility in 2 M NaOH at different temperatures and pressures

B2. Calculation of electrolyte conductivity in sodium hydroxide solutions

The electrolyte conductivity k_{apl} is approximated by fitting a polynomial equation to NaOH conductivity vs NaOH concentration data [CRC handbook, 1986] and a temperature coefficient for conductivity increase of 0.023 per degree K (rule of thumb) rise in temperature [Oloman, 1996]

$$k_{apl} = (0.0726 + 19.576 C_{NaOH} - 3.035 C_{NaOH}^2) (1 + 0.023 (T - 293)) \quad (B-5)$$

A surface plot of electrolyte conductivity (NaOH) based on equation (B-5) is given in Figure B.4.

Figure B.4 Electrolyte conductivity (NaOH) at different concentrations and temperatures

APPENDIX C

Single-cell reactor model equations

For the ease of understanding the modelling algorithm for a single-cell reactor many of the equations discussed previously in Chapter 5 equations have been shown again. Based on their nature, the equations could be clustered into separate groups.

The parameters used in modelling the single-cell reactor for peroxide generation are given in Chapter 5 (Table 5.2).

C1. Vapour pressure of water and the reactor pressure

The vapour pressure of NaOH solution $< 10\%_w$ [Hooker, 1977]) may be approximated from the Antoine's equation for pure water [Reklaitis, 1983] using:

$$P_{H_2O} = e^{\left(16.5362 - \frac{3985.44}{T - 38.9974}\right)} \quad kPa \quad (C-1)$$

The O_2 pressure may be calculated by subtracting the vapour pressure of water from the reactor pressure:

$$P_{O_2} = P - P_{H_2O} \quad kPa (abs.) \quad (C-2)$$

C2. Liquid and gas densities

Liquid density ($kg\ m^{-3}$) for the electrolyte (NaOH) is calculated by least square fitting to data for NaOH density versus concentration [CRC handbook, 1986]:

$$\rho_L = 1000(1 + 0.04C_{Na+}) \quad kg\ m^{-3} \quad (C-3)$$

Gas density ($kg\ m^{-3}$) is estimated using the combined gas law (ignoring the water vapour):

$$\rho_G = \frac{M_{O_2} P_{O_2}}{RT} \quad kg\ m^{-3} \quad (C-4)$$

C3. Liquid and gas viscosities

Liquid viscosity is calculated by least square fitting to data for NaOH viscosity versus temperature and concentration [CRC handbook, 1986]:

$$\mu_L = 0.001(1 + 0.5 C_{Na+}) 10^{-10.73 + 1828/T + 0.01966T - 1.466e-5 T^2} \quad kg\ m^{-1}\ sec^{-1} \quad (C-5)$$

Gas (O₂) viscosity is calculated by least square fit to data for O₂ viscosity versus temperature [CRC handbook, 1986]:

$$\mu_G = 1e-6[18.11 + 0.6632 T - (1.879e-4)T^2] \quad kg\ m^{-1}\ sec^{-1} \quad (C-6)$$

C4. Diffusivities of various species

The diffusivities of HO₂⁻, OH⁻, Na⁺ & O₂ in NaOH are calculated using Stokes-Einstein equation ($D\mu/T = \text{constant}$) [Oloman, 1996]:

$$D_{HO_2^-} = \frac{0.001D_{HO_2^-}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (C-7)$$

$$D_{OH^-} = \frac{0.001D_{OH^-}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (C-8)$$

$$D_{Na^+} = \frac{0.001D_{Na^+}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (C-9)$$

$$D_{O_2} = \frac{0.001D_{O_2}^0 T}{298\mu_L} \quad m^2\ s^{-1} \quad (C-10)$$

The effective diffusivities of HO₂⁻ and OH⁻ ions in the diaphragm are determined by the porosity of diaphragm and according to Neale and Nader (1973) is given by:

$$D_{dHO_2^-} = \frac{2D_{HO_2^-}\epsilon_d}{3 - \epsilon_d} \quad m^2\ s^{-1} \quad (C-11)$$

$$D_{\text{dOH}^-} = \frac{2D_{\text{OH}^-}\varepsilon_d}{3 - \varepsilon_d} \quad m^2 s^{-1} \quad (\text{C-12})$$

C5. Henry's constant

For mildly soluble gases the gas (O_2) to liquid (NaOH) equilibrium is defined using Henry's law [Treybal, 1993]:

$$C_{\text{O}_2} = \frac{(P_{\text{O}_2}/101)}{H} \quad kmol m^{-3} \quad (\text{C-13})$$

where H is the Henry's constant for oxygen dissolution in NaOH solution (Appendix B) and is given by:

$$H = \frac{H_0}{(C_{\text{NaOH}, \text{O}_2} / C_{\text{H}_2\text{O}, \text{O}_2})} \quad kmol kg^{-1} m^{-2} sec^2 \quad (\text{C-14})$$

and H_0 is the Henry's constant for O_2 dissolution in H_2O (Appendix B) and is given by:

$$H_0 = e^{\left[\frac{0.046T^2 + 203.35T \ln(T/298) - (299.378 + 0.092T)(T - 298) 20.591e3}{8.3144T} \right]} \quad kmol kg^{-1} m^{-2} sec^2 \quad (\text{C-15})$$

$C_{\text{NaOH}, \text{O}_2} / C_{\text{H}_2\text{O}, \text{O}_2}$ is calculated using the Sechenov equation (Appendix B).

C6. Specific surface area of the graphite felt cathode

Specific surface is the area per unit volume of the graphite felt and is given by:

$$s = 4 \frac{(1 - \varepsilon_b)}{d_f} \quad m^{-1} \quad (\text{C-16})$$

Equation (C-16) may be derived from the fact that each strand of felt fibre is assumed to be a cylinder with surface area given by $\pi d_f \Delta l$, where Δl is the length of the fibre. The volume of the fibre strand is given by $\pi d_f^2 \Delta l / 4$. And the volume of cathode bed carrying the fibre strand volume is given by $(\pi d_f^2 \Delta l / 4) / (1 - \varepsilon_b)$. So dividing the surface area of the strand by the volume of cathode bed carrying the equivalent surface area one arrives at (C-16). If the particles in the cathode bed were spherical instead of being

cylindrical in shape a factor of 6 would be found in the numerator of equation (C-16) instead of 4. So the equivalent particle diameter is arrived at by multiplying the fibre diameter by the ratio (i.e. 6/4) and is given by:

$$d_e = \frac{6}{4} d_f \quad m \quad (C-17)$$

C7. Fluid dynamics and mass transfer in the reactor

To establish the mechanism of gas to liquid to solid mass transfer it is necessary to understand the two-phase gas and liquid dynamics in the reactor.

To establish a complete model for the single-cell reactor, let us start with the basics of two-phase flow of gas (O₂) & liquid (H₂O and NaOH) followed by the gas (O₂) to solid (graphite) mass transfer in the reactor.

Single-phase pressure gradients of gas and liquid can be calculated using Ergun's equation [Bird et al, 1994]. The single-phase equations are then combined to calculate the two-phase pressure drop.

Single-phase pressure gradients for gas and liquid are given by:

$$\nabla P_G = (150 + 1.75 \text{Re}_G) \mu_G U_G (1 - \varepsilon_b)^2 d_e^2 \varepsilon_b^3 \quad kg \, m^{-2} \, sec^{-2} \quad (C-18)$$

$$\nabla P_L = (150 + 1.75 \text{Re}_L) \mu_L U_L (1 - \varepsilon_b)^2 d_e^2 \varepsilon_b^3 \quad kg \, m^{-2} \, sec^{-2} \quad (C-19)$$

The two-phase pressure gradient equation is given by the correlation of Sato et al (1973):

$$\nabla P_{LG} = \nabla P_L \left(1.30 + 1.85 \left(\frac{\nabla P_L}{\nabla P_G} \right)^{-0.425} \right)^2 \quad kg \, m^{-2} \, sec^{-2} \quad (C-20)$$

The liquid hold up is determined from the work of Specchia and Baldi (1977):

$$h_l = 3.86 \text{Re}_L^{0.545} \text{Ga}_L^{-0.42} \left(\frac{s d_e}{\varepsilon_b} \right)^{0.65} \quad (C-21)$$

where a_L is the modified Galileo number given by:

$$Ga_L = d_e^3 \rho_L \left(\frac{\rho_L g_a + \nabla P_{LG}}{\mu_L^2} \right) \quad (C-22)$$

The gas and liquid phase mass transfer capacities are calculated from Reiss (1967):

$$k_{ls} = 0.0173 (\nabla P_{LG} U_L)^{0.5} \quad s^{-1} \quad (C-23)$$

$$k_{gs} = 2 + 0.69 (\nabla P_{LG} U_G)^{0.67} \quad s^{-1} \quad (C-24)$$

The liquid to solid transfer capacity is calculated from the work of Satterfield (1975):

$$k_{ls} = \frac{0.429 Re_L^{0.5} Sc_L^{0.33} s^2 D_L}{h_l} \quad s^{-1} \quad (C-25)$$

The overall capacity coefficient for mass transfer for oxygen from gas to graphite felt surface, based on film theory [Treybal, 1993] is given by:

$$k_o = \left(\frac{1}{k_g} + \frac{H}{k_l} + \frac{H}{k_s} \right) \quad m \, s^{-1} \quad (C-26)$$

where H is the Henry's constant for gas-liquid equilibrium or O₂ dissolution in NaOH in the current case.

Equation (C-26) is valid based on the assumption that the specific gas/liquid and liquid/solid interfacial areas are equal to the specific surface area of the solid particle in the bed.

Equations (C-18) to (C-26) have been shown as they provide a physical understanding of the mechanism of pressure drop and mass transfer capacities in any packed bed reactor. However, for accuracy it is better to use a correlation of pressure drop, gas hold up and mass transfer capacities for the actual reactor at hand. Hodgson and Oloman (1999) developed correlations for two-phase pressure gradient and mass transfer capacities for graphite felts with 1M NaOH at ca. 293-313 K.

The two-phase pressure gradient based on Hodgson and Oloman's (1999) correlation is given by:

$$\nabla P_{LG} = \left(\frac{\text{liq}}{t_b w} \right) \left(0.36 + 1.182 \left(\frac{g}{\text{liq}} \right)^{0.618} \right)^2 \Delta z \quad \text{kg m}^{-2} \text{sec}^{-2} \quad (\text{C-27})$$

The liquid hold up is given by:

$$h_l = 1 - 0.907 \left(\frac{\text{liq}}{t_b w} \right)^{-0.362} \left(\frac{g}{t_b w} \right)^{0.301} \quad (\text{C-28})$$

The overall mass transfer coefficient for oxygen is given by:

$$k_o = 5.9 \left(\frac{\text{liq}}{t_b w} \right)^{0.372} \left(\frac{g}{t_b w} \right)^{0.301} \left(\frac{1}{s} \right) \quad \text{m s}^{-1} \quad (\text{C-29})$$

where liq, g are mass flow rate of liquid and gas through the cathode bed and s is the superficial electrode area of the cathode bed. Hodgson and Oloman (1999) developed correlations for mass transfer capacity (k_{os}). As specific surface area s can be calculated from equation (C-16), mass transfer coefficient for O_2 can be derived from equation (C-29).

Assuming a constant film thickness, the mass transfer coefficient for perhydroxyl ions may be approximated by:

$$k_{HO_2^-} = \frac{k_o D_{HO_2^-}}{D_{O_2}} \quad \text{m s}^{-1} \quad (\text{C-30})$$

C8. Effective electrode and electrolyte conductivities

The electrolyte conductivity is approximated by fitting a polynomial equation to NaOH conductivity vs NaOH concentration data [CRC handbook, 1986] and a temperature coefficient for conductivity increase of 0.023 per degree K rise in temperature [Oloman, 1996]:

$$k_{apl} = (0.0726 + 19.576 C_{Na^+} - 3.035 C_{Na^+}^2) (1 + 0.023 (T - 293)) \quad \text{S m}^{-1} \quad (\text{C-31})$$

The effective electrolyte conductivity assuming uniform electrolyte concentration in the diaphragm (k_{apd}) and the graphite felt cathode (k_{apb}) is calculated from the work of Neale and Nader (1973):

$$k_{apd} = \frac{2 k_{apl} \varepsilon_d}{(3 - \varepsilon_d)} \quad S m^{-1} \quad (C-32)$$

$$k_{apb} = \frac{2 k_{apl} \varepsilon_b h_1}{(3 - \varepsilon_b h_1)} \quad S m^{-1} \quad (C-33)$$

The effective electrode conductivity of the cathode matrix is calculated from the correlation of Oloman et al (1991):

$$k_{aps} = 10 + 2800 \left(\frac{1 - \varepsilon_b}{\varepsilon_o} \right)^{1.55} \quad S m^{-1} \quad (C-34)$$

C9. Current densities and potentials on the cathode and anode

Assuming the total superficial current density on the cut section (Figure 5.8) of the anode as i $kA m^{-2}$ (not known a priori), the superficial current density on the anode due to perhydroxyl ion oxidation (2.10) is the sum of diffusive, convective and migrative flux and is given by:

$$i_{HO2^-} = \frac{(D_{dHO2^-} + D_{ed})(C_{HO2^-} - 0)F}{t_d} + \frac{0.001 D_{dHO2^-} F^2 C_{HO2^-} i}{k_{apd} RT} \quad kA m^{-2} \quad (C-35)$$

Convective flux may be accounted for by introducing an eddy diffusivity term D_{ed} in the diffusive component in equation (C-35) however presently in the model D_{ed} is kept as zero because of the difficulty of measuring it.

The superficial current density due to hydroxyl ion oxidation (2.11) on the anode is given by:

$$i_{OH^-} = i - i_{HO2^-} \quad kA m^{-2} \quad (C-36)$$

Appendix C

Likewise the superficial current density on the anode due to diffusive, convective and migrative flux of hydroxyl ions may be derived by the following equation:

$$i_{OH^-} = \frac{(D_{dOH^-} + D_{ed})(C_{OH^-} - C_{aOH^-})F}{t_d} + 0.001D_{dOH^-}F^2i \left(\frac{C_{OH^-} + C_{aOH^-}}{2k_{apd}RT} \right) \text{ kA m}^{-2} \quad (C-37)$$

where C_{aOH^-} is the concentration of hydroxyl ions at the anode. This hydroxyl concentration is not known a priori and may be calculated by rearranging equation (C-37) in terms of C_{aOH^-} .

To account for the migrative flux of hydroxyl ions in (C-37), the concentration is averaged across the diaphragm i.e. $(C_{OH^-} + C_{aOH^-})/2$.

Equation (C-37) is used to derive the equation for hydroxyl ion concentration (C_{aOH^-}) at the anode using the following equations:

$$\text{coef}_1 = \frac{(D_{dOH^-} + D_{ed})F}{t_d} \quad (C-38)$$

$$\text{coef}_2 = \frac{D_{dOH^-}F^2i}{2k_{apd}RT} \quad (C-39)$$

$$C_{aOH^-} = \frac{(i_{OH^-} - (\text{coef}_1 + \text{coef}_2)C_{OH^-})}{(\text{coef}_2 - \text{coef}_1)} \quad \text{kmol m}^{-3} \quad (C-40)$$

The equilibrium potential for reaction (2.3) on the cathode is given by:

$$V_{rc1} = -0.076 - \left(\frac{RT}{2F} \right) \ln \left(\frac{C_{HO2^-} C_{OH^-}}{P_{O_2}} \right) \quad V \quad (C-41)$$

and for reaction (2.4) is given by:

$$V_{rc2} = 0.878 - \left(\frac{RT}{2F} \right) \ln \left(\frac{C_{OH^-}^3}{C_{HO2^-}} \right) \quad V \quad (C-42)$$

The major reaction occurring on the anode is the oxidation of hydroxyl ions (2.11). The perhydroxyl ions reaching the anode are assumed to be completely oxidized in the model.

Appendix C

The equilibrium potential for hydroxyl ion oxidation (2.11) is given by:

$$V_{ra} = 0.401 - \left(\frac{RT}{4F} \right) \ln \left(\frac{C_{aOH^-}}{P_{O_2}} \right) \quad V \quad (C-43)$$

The overpotential on the anode due to reaction (2.11) is given by:

$$\eta_a = a_a + b_a \log(i_{OH^-}) \quad V \quad (C-44)$$

where a_a and b_a are Tafel constants

The diaphragm potential drop assuming uniform electrolyte concentration in diaphragm is given by:

$$V_d = 1000 \frac{it_d}{k_{apd}} \quad V \quad (C-45)$$

Oxidation of perhydroxyl ions on the anode is not considered for the purpose of voltage balance.

The real current density based on the Butler-Volmer equation [Pickett, 1983] on the cathode for perhydroxyl ion formation (2.3) is given by:

$$j_{HO_2^-} = \frac{2F k^0_1 \exp \left[\left(\frac{-E_{a1}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_O C_{O_2} \exp \left[\left(\frac{-\alpha_1 F}{RT} \right) (\phi_s - \phi_b - V_{rc1}) \right]}{k_O + k^0_1 \exp \left[\left(\frac{-E_{a1}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_O C_{O_2} \exp \left[\left(\frac{-\alpha_1 F}{RT} \right) (\phi_s - \phi_b - V_{rc1}) \right]} \quad kA \, m^{-2} \quad (C-46)$$

where k^0_1 is the rate constant for reaction (2.3) at 288 K.

Similarly for perhydroxyl ion reduction reaction (2.4) the real current density is given by:

$$j_{OH^-} = \frac{2F k^0_2 \exp \left[\left(\frac{-E_{a2}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_{HO_2^-} C_{HO_2^-} \exp \left[\left(\frac{-\alpha_2 F}{RT} \right) (\phi_s - \phi_b - V_{rc2}) \right]}{k_{HO_2^-} + k^0_2 \exp \left[\left(\frac{-E_{a2}}{R} \right) \left(\frac{1}{T} - \frac{1}{288} \right) \right] k_{HO_2^-} C_{HO_2^-} \exp \left[\left(\frac{-\alpha_2 F}{RT} \right) (\phi_s - \phi_b - V_{rc2}) \right]} \quad kA \, m^{-2} \quad (C-47)$$

where k_2^0 is the rate constant for reaction (2.4) at 288 K and ϕ_s and ϕ_b are the electrode and electrolyte potential respectively at any point in the graphite felt cathode (Figure C.2).

C10. Voltage (a.k.a. charge) balance equations

The voltage balance equations on the graphite felt 3D cathode (Figure C.2) are a complex function of electrode, electrolyte potential and current densities for perhydroxyl ion formation (2.3) and reduction (2.4) and are given by the second order non-linear differential equation:

$$\nabla^2(\phi_s - \phi_b) = -s \left(\frac{1}{k_{aps}} + \frac{1}{k_{apb}} \right) j \quad (C-48)$$

Equation (C-48) may be derived by differentiating the equation for Ohm's law in electrode (C-49) and electrolyte phase (C-50) and taking the divergence of the current transferred from the electrode to electrolyte phase (C-51):

$$\nabla \phi_s = - \frac{i_s}{k_{aps}} \quad (C-49)$$

$$\nabla \phi_b = - \frac{i_b}{k_{apb}} \quad (C-50)$$

$$\nabla \cdot i_s = -\nabla \cdot i_b = s j_{\text{cathode}} \quad (C-51)$$

where i_s and i_b are the current densities in electrode and electrolyte phase respectively.

or equivalently for one dimension (C-48) reduces to:

$$\frac{d^2(\phi_s - \phi_b)}{dx^2} = s \left(\frac{1}{k_{aps}} + \frac{1}{k_{apb}} \right) j \quad (C-52)$$

where $j_{\text{cathode}} = f(\phi_s, \phi_b)$ is given by:

$$j_{\text{cathode}} = j_{\text{HO}_2\cdot} + j_{\text{OH}\cdot} \quad kA\ m^{-2} \quad (C-53)$$

Equation (C-52) is equivalent to solving the following four 1st order D.E.s:

$$Zb = \frac{d\phi_b}{dx} \quad (C-54)$$

$$\text{boundary condition: } \phi_b = V_{cf} \quad \text{at } x = 0 \quad (\text{C-55})$$

$$Z_s = \frac{d\phi_s}{dx} \quad (\text{C-56})$$

$$\text{boundary condition: } \phi_s = 0 \quad \text{at } x = t_b \quad (\text{C-57})$$

$$\frac{dZ_b}{dx} = \frac{-sj}{k_{apb}} \quad (\text{C-58})$$

$$\text{boundary condition: } d\phi_b/dx = -i/k_{apb} \quad \text{at } x = 0 \quad (\text{C-59})$$

$$\frac{dZ_s}{dx} = \frac{sj}{k_{aps}} \quad (\text{C-60})$$

$$\text{boundary condition: } d\phi_s/dx = 0 \quad \text{at } x = 0 \quad (\text{C-61})$$

Equations (C-48) to (C-61) cannot be solved simply as the current density (*i*) on the anode is not known, a priori. Thus the superficial current density (*i*) is guessed and the voltage balance iterated to arrive at the solution of the differential equation (C-48). The solution methodology is discussed in the voltage balance (Figure C.2).

Figure C.2 provides a flow sheet for the voltage balance i.e. to solve the Poisson's equation in the 3D cathode given by (C-52). The Poisson's equation is a second order non-linear differential equation (C-52) and is solved by converting it into four first order equations given by (C-54), (C-56), (C-58) & (C-60). These four first order equations have their respective boundary conditions in equation (C-55), (C-57), (C-59) & (C-61). The boundary condition (C-57) is known at $x = t_b$ and not at $x = 0$. So the value of the boundary condition (C-57) at $x = 0$ has to be guessed to solve the differential equations. The four first order differential equations (C-54), (C-56), (C-58) & (C-60) are solved using 5th order Runge-kutta and a shooting method that aims for a boundary condition for cathode matrix potential, ϕ_s at $x = t_b$. If this potential ϕ_s is found to be zero then the total current transferred from the electrolyte to the cathode matrix is calculated. If this transferred current matches the initial guessed current (*i*) on the anode then the voltage balance is converged, else one keeps on repeating these steps till the problem is solved.

ϕ_s, ϕ_b	= electrode, electrolyte potential	V
η_a	= anode overpotential	V
V_{cf}	= cathode face potential	V
V_d	= diaphragm IR drop	V
V_r	= reactor voltage	V
V_{ra}	= equilibrium voltage for reaction (2.10) on the anode	V
k_{apb}	= effective electrolyte conductivity	$S\ m^{-1}$
k_{aps}	= effective matrix (felt) conductivity	$S\ m^{-1}$
$j_{cathode}$	= real current density on the 3D cathode due to reaction (2.3) & (2.4)	$kA\ m^{-2}$
s	= specific surface area of 3D cathode	m^{-1}
l_e	= length of the reactor	m
t_b	= thickness of cathode bed (graphite felt)	m
Δz	= thickness of the cross-section in Figure 5.8	m
w	= width of the reactor	m

Figure C.1 Voltage balance for one length increment on a single-cell reactor

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Figure C.2 Flow chart for voltage balance for one length increment on a single cell reactor

C11. Material balance equations

Figure C.3 Differential section of Figure 5.8

The concentrations of perhydroxyl, hydroxyl and sodium ions at the exit of the cut section in Figure C.3 are given by:

$$C'_{HO_2^-} = \left(C_{HO_2^-} + \frac{w\Delta z(\sum st_b j_{HO_2^-} - \sum st_b j_{OH^-} - i_{HO_2^-})}{2F liq/\rho_L} \right) \quad kmol m^{-3} \quad (C-62)$$

$$C'_{OH^-} = \left(C_{OH^-} + \frac{w\Delta z(\sum st_b j_{HO_2^-} + 3\sum st_b j_{OH^-} - 2i_{OH^-})}{2F liq/\rho_L} \right) \quad kmol m^{-3} \quad (C-63)$$

$$C'_{Na^+} = C_{Na^+} \quad kmol m^{-3} \quad (C-64)$$

The concentrations of perhydroxyl, hydroxyl and sodium ion calculated in equations (C-62), (C-63) & (C-64) are initialized again in the following equations (C-65), (C-66) & (C-67) to do voltage, material and energy balance over the next section of the reactor.

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$$C_{\text{HO}_2^-} = C'_{\text{HO}_2^-} \quad \text{kmol m}^{-3} \quad (\text{C-65})$$

$$C_{\text{OH}^-} = C'_{\text{OH}^-} \quad \text{kmol m}^{-3} \quad (\text{C-66})$$

$$C_{\text{Na}^+} = C'_{\text{Na}^+} \quad \text{kmol m}^{-3} \quad (\text{C-67})$$

$\Sigma s t_b j_{\text{HO}_2^-}$ is the total current transferred from the electrolyte to the cathode matrix due to reaction (2.3) in the cut section of Figure C.3. The material balances are based on the net currents transferred in reactions (2.3) & 2.4) due to HO_2^- and OH^- ions.

The oxygen flow exiting the cut section of Figure C.3 is calculated by subtracting the oxygen used in reaction (2.3):

$$g' = g - \frac{M_{\text{O}_2} (\Sigma s t_b j_{\text{HO}_2^-}) w \Delta z}{2F} \quad \text{kg s}^{-1} \quad (\text{C-68})$$

$$g = g' \quad \text{kg s}^{-1} \quad (\text{C-69})$$

The oxygen generated on the anode is not accounted for in equation (C-68) as in the single cell reactor it flows through the dummy anode in Figure 5.8 and does not contribute to any further reactions.

C12. Energy balance equations

From Figure C.3,

$$\text{heat input} + \text{heat generation} = \text{heat output} + \text{heat accumulation} \quad (\text{C-70})$$

At steady state the accumulation term is zero and therefore,

$$\text{heat output} - \text{heat input} = \left[(\text{liq}) c_1 (T' - T) - \frac{1000 \left(\frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) (g) \Delta H_{\text{evap}}}{M_{\text{O}_2}} \right] \text{kJ s}^{-1} \quad (\text{C-71})$$

Ignoring entropy effects, the heat generation rate may be approximated by:

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$$\text{heat generation} = (V_r + V_{rc1} - V_{ra}) i w \Delta z \quad \text{kJ s}^{-1} \quad (\text{C-72})$$

Equating (C-71) & (C-72),

$$T' = T + \frac{((V_r + V_{rc1} - V_{ra}) i w \Delta z)}{(liq) c_1} - \frac{1000 \left(\frac{P_{H_2O}}{P - P_{H_2O}} \right) (g) \Delta H_{\text{evap}}}{M_{O_2} (liq) c_1} \quad K \quad (\text{C-73})$$

where ΔH_{evap} is the heat of vaporization ($42.85 \text{ kJ mol}^{-1}$ averaged from 273 -373 K [Atkins, 1973]) for water.

Water vapour pressure P_{H_2O} is a function of temperature of the reactor and is calculated at the local temperature prevailing in the reactor with the assumption that the temperature does not significantly differ in two length increments in Figure 5.8

The temperature may be reinitialized to do the voltage, material & energy balances on the next length increment of the reactor.

$$T = T' \quad K \quad (\text{C-74})$$

The heat carried by O_2 is neglected as it contributes little to the overall energy balance.

C13. Reactor pressure equation

The two phase pressure drop in the cut section (Figure C.3) is given by:

$$\Delta P_{LG} = \nabla P_{LG} \Delta z \quad Pa \quad (\text{C-75})$$

The new reactor pressure may be calculated by subtracting pressure drop in the reactor from the original pressure:

$$P' = P - 0.001 \Delta P_{LG} \quad kPa \quad (\text{C-76})$$

The pressure may be reinitialized to do the voltage, material & energy balances on the next section in the reactor.

$$P = P' \quad kPa \quad (C-77)$$

∇P_{LG} is calculated using equation (C-25) for two-phase pressure gradient in the reactor.

C14. Total reactor current

Reactor current is given by:

$$I_{\text{reactor}} = I_{\text{reactor}} + I \quad \text{Amperes} \quad (C-78)$$

C15. Current efficiency for peroxide generation

The current efficiency for perhydroxyl generation may be calculated from the following equation:

$$C.E. = \frac{2000F C_{\text{HO}_2}(\text{liq}/\rho_L)}{I_{\text{reactor}}} \quad (C-79)$$

C16. Specific electrochemical energy for peroxide generation

The specific energy for perhydroxyl generation may be calculated from the following equation

$$S.E. = \frac{2FV_r}{(3600)(34)C.E.} \quad kWh\ kg^{-1} \quad (C-80)$$

The algorithm for solving the single cell reactor model is provided in Figure C.4

Figure C.4 Solution algorithm for the complete single-cell reactor model

The code for solving the single cell reactor model of Figure C.4 is given below.

Single cell reactor model code in Fortran 77

The code for modelling the single cell reactor as discussed in Chapter 5 is given below.

C This code does modelling of the hydrogen peroxide single cell reactor
 C A prefix **x** is attached to some variables in the model (Chapter 5)
 C to make the variables **real**

Implicit Double Precision(A-H,O-Z)

Integer Flag

```
DOUBLE PRECISION xkapd(100),di1(100),di2(100),di3(100)
DOUBLE PRECISION c1(100),c2(100),c3(100),c4(100),p(100)
DOUBLE PRECISION xib2(100),xi1(100),xi2(100),t(100)
DOUBLE PRECISION delx,xib1(100),td
DOUBLE PRECISION phis(1),ya(4),x(100),yb(100)
DOUBLE PRECISION vb(100,100),vs(100,100),vc(100,100),vcf(100)
DOUBLE PRECISION xj1(100,100),xj2(100,100)
DOUBLE PRECISION die1(100),die2(100)
DOUBLE PRECISION c2a(100),vra(100),xna(100),vd(100)
DOUBLE PRECISION g(100),xii(2),xiii(2),fx(2)
DOUBLE PRECISION rol(100),visl(100),visg(100)
DOUBLE PRECISION ul(100),ug(100),dpl(100),dpg(100)
DOUBLE PRECISION rel(100),reg(100),scl(100),dp(100),delp(100)
DOUBLE PRECISION gal(100),hl(100)
DOUBLE PRECISION di4(100)
DOUBLE PRECISION xkapl(100)
DOUBLE PRECISION xjlim1(100)
DOUBLE PRECISION xi(100)
```

```
common/Blk1/k,xkapb(100)
```

```
common/Blk2/Hstart,Hmin,Hmax,NE
```

```
common/Blk3/tb,eps,np,delx,vcfk,xiinx
```

```
common/Blk4/xkk1,xkk2,bb1,bb2,xkok(100),xkHO2(100),
+ xk1,xk2,vr1(100),vr2(100),xkaps(100),s
```

Appendix C

Open(Unit=1,file ='singlecell.out', STATUS='UNKNOWN')

C **Input data**

C 1-perhydroxyl, 2-hydroxyl, 3-Na, 4-O2

C Liquid and gas heat capacities are given by cl and cg respectively
(kJ/kg/K)

data cl,cg/4.d0,0.9d0/

C c1(k),c2(k),c3(k)& c4(k) are the concentrations of perhydroxyl ion,
C hydroxyl ion Na⁺ and O2 respectively

data c1(1),c2(1),c3(1)/1.d-6,1.d0,1.d0/

C dif1, dif2, dif3, dif4 diffusivity at infinite dilution, m2/s

C 1-perhydroxyl, 2-hydroxyl, 3-Na, 4-O2

data dif1,dif2,dif3,dif4/1.5d-9,5.3d-9,1.3d-9,2.4.d-9/

C Diameter of the graphite felt fibre, m

data df/2.d-5/

C Porosity of compressed graphite felt or cathode bed porosity (eb)

C Diaphragm porosity is given by ed

data eb,ed/0.90d0,0.8d0/

C Porosity of uncompressed graphite felt is given by eo

data eo/0.95 d0/

C eps = convergence criterion for desolv sub-routine

data/eps/1.d-3/

C eps1 = current density convergence criterion

data eps1/1.d-5/

C eps2 = cathode face voltage convergence criterion

data eps2 /1.d-2/

C Oxygen flow rate is given by g(k) (kg/s)

data g(1)/17.d-6/

C hl = liquid hold up

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- $h_{min} = 1.d-6$
 $h_{max} = 1.d-5$
 $h_{start} = h_{max}$
- C Liquid flow rate per reactor is given by x_l (kg/s)
data $x_l/3.36d-4/$
- C x_{le} = reactor length, metre
data $x_{le}/0.12d0/$
- C x_{ii} = total superficial current density, kA/m²
- C x_{ib1}, x_{ib2} = superficial current densities at cathode for
C reaction (2.3) and (2.4) kA/m² respectively
- C x_{i1}, x_{i2} current densities for peroxide, hydroxide on the anode, A/m²
- C x_{j1}, x_{j2} local real current density for reaction 1,2 A/m²
- C k = length increment, km = mass transfer coefficient, m/s
- C x_{k01}, x_{k02} = electrochemical rate constants for cathode reactions, 1, 2 m/s
 $x_{k1} = 5.d-7$
 $x_{k2} = 1.6d-9$
- C x_{mw} = molecular weight of O₂
data $x_{mw}/32.d0/$
- C $n - 1$ = no. of length increments of reactor
data $n/21/$
- C n_e = no. of differential equations to be solved
data $n_e/4/$
- C $n_p - 1$ = no. of thickness increments in which differential
C equation is to be solved
data $n_p/21/$
- C p = pressure, kPa
data $p(1)/804/$
- C t = temp K
data $t(1)/298.d0/$
- C t_b = bed thickness, m

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- data tb/3.2d-3/
- C td = diaphragm thickness, m
data td/3.d-4/
- C vb = potential of liquid, vs = potential of solid
- C vc = vs - vb electrode potential
- C vcf = electrode potential at the face of cathode bed
- C vr = reactor voltage, V
data vr/3.d0/
- C w = width of the reactor, m
data w/2.5d-2/
- C ded = eddy diffusivity through diaphragm, m²/s
data ded/0/
- C FAR = Faraday constant, R = gas constant
data FAR,R/96486.d0,8.314d0/
- C ximin, ximax - min, and max, range of total current in the bed A/m²
data ximin,ximax/1000.d0,30000.d0/
- C **Input data complete**
- C Ireactor is the total current through the reactor
- C xib1t is the total current through the bed for reaction 2.3
- C xib2t is the total current through the bed for reaction 2.4
- C **Initializing the parameters**
Ireactor = 0.d0
xib1t = 0.d0
xib2t = 0.d0
xilt = 0.d0

del = xle/(n-1)
delx = tb/(np-1)
- C **Main program begins**
- C calculate the values for transport phenomena

DO 85 K = 1,N

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$$rol(k) = 1000.d0*(1.d0 + 0.04d0*c3(k))$$

C Liquid and gas viscosities are given by visl(k) and visl(g) (Pa s)

$$+ \quad p1 = -1.073d1 + 1.828d3/t(k) + 1.966d-2*t(k) - 1.d-6*1.466d1*(t(k)**2)$$

$$visl(k) = 1.d-3*(1+0.5d0*c3(1)*10.d0**p1)$$

$$visg(k)=1.d-6*(1.811d1+6.632d-1*t(k)-1.d-6*1.879d2*(t(k)**2))$$

C Diffusion coefficient for the given electrolyte viscosity is given by
C di1(k), di2(k), di3(k) & di4(k) (m²/s) where
C 1-perhydroxyl, 2-hydroxyl, 3-Na, 4-O₂

$$di1(k) = dif1*t(k)*1.d-3/(visl(k)*298.d0)$$

$$di2(k) = dif2*t(k)*1.d-3/(visl(k)*298.d0)$$

$$di3(k) = dif3*t(k)*1.d-3/(visl(k)*298.d0)$$

$$di4(k) = dif4*t(k)*1.d-3/(visl(k)*298.d0)$$

C Henry's constant of O₂ in H₂O is give by Ho (Troman's equation)
+ Ho=exp((0.046*(T**2)+203.35*T log(T/298)-(299.378+0.092*T)*T-298)-20.591e3)/(8.3144*T))

C Henry's constant for O₂ in NaOH is given by H (Sechenov eqn.)
H = Ho/1.59

C Vapour pressure of water kPa is given by pH₂O
pH₂O(k) = exp(16.5362- 3985.44/(t(k) -38.9974))
pO₂(k) = p(k) - pH₂O(k)

C O₂ concentration in NaOH solution assuming O₂ in liquid to be in
C equilibrium with the gas is given by c₄(k) kmol/m³

$$c4(k) = pO2(k)/(H*101.d0)$$

C Equivalent diameter of the graphite felt cathode is given by de (m)
de = 1.5*df

C Specific surface area of the cathode bed is given by s (m²/m³)
s = 4*(1-eb)/df

C Press gradient (Pa/m) in the reactor is given by delp(k)

$$delp(k) = 100*(xl/(tb*w))*(0.36+1.182*((g(k)/xl)**0.618)**2)*del$$

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- C Liquid hold up in the reactor is given by $hl(k)$
 $hl(k) = 1.d0 - 0.907 * ((xl/(tb*w))^{**}(-0.362d0)) * ((g(k)/(tb*w))^{**}0.301d0)$
+
- C Mass transfer coefficient for O₂ through NaOH in the reactor is
C given by $xkok(k)$ (m/s)
 $xkok(k) = 5.9 * ((xl/(tb*w))^{**}0.372) * ((g(k)/(tb*w))^{**}0.301)/s$
- C Approximate mass transfer coefficient of HO₂⁻ ions in NaOH
C solution is given $xkHO2(k)$ (m/s)
 $xkHO2(k) = xkm4(k) * di1(k)/di4(k)$
- C Mass transfer limited current density for peroxide generation
C reaction (2.3) is given by $xjlim1(k)$ (A/m²)
 $xjlim1(k) = 1000.d0 * 2.d0 * FAR * xkok(k) * c4(k)$
- C Electrolyte conductivity is given by $xkapl(k)$ (S/m)
 $xkapl(k) = 0.0726 + 19.576 c3(k) - 3.035 c3(k)^{**}2$
- C Diaphragm conductivity is given by $kapd(k)$ (S/m)
 $xkapd(k) = 2.d0 * xkapl(k) * ed / (3.0 - ed)$
- C Compressed graphite felt conductivity is given by $kaps(k)$ (S/m)
 $xkaps(k) = 10.d0 + 2800.d0 * (((1 - eb)/eo)^{**}1.55d0)$
- C Effective electrolyte conductivity in the graphite felt is given
C by $kapb(k)$ (S/m)
 $xkapb(k) = 2.d0 * xkapl(k) * eb * hl(k) / (3.d0 - eb * hl(k))$
- C Equilibrium voltage for perhydroxyl generation reaction (2.3)
C is given by $vr1(k)$ (V)
 $coef1 = \log((c1(k) * c2(k)) / pO2(k) / 101)$
 $vr1(k) = -0.076d0 - (R * t(k) / (2.d0 * FAR)) * coef1$
- C Equilibrium voltage for perhydroxyl reduction reaction (2.4)
C is given by $vr2(k)$ (V)
 $coef2 = \log((c2(k)^{**}3) / c1(k))$
 $vr2(k) = 0.878 - (R * t(k) / (2.d0 * FAR)) * coef2$
- C Accounting for increased rate constant with temperature for
C reaction (2.3)
 $xk1 = xk01 * \exp(-25530 / R * (1/t(k) - 1/288))$

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C Accounting for increased rate constant with temperature for
 C reaction (2.4)

$$xk2 = xk02 * \exp(-25530/R * (1/t(k) - 1/288))$$

C Defining a few constants to be simplify calculations

$$bb1 = -0.546d0 * FAR/R/t(k)$$

$$bb2 = -0.263d0 * FAR/R/t(k)$$

$$xkk1 = 1000.d0 * 2.d0 * FAR * xk1 * xkok(k) * c4(k)$$

$$xkk2 = 1000.d0 * 2.d0 * FAR * xk2 * xkHO2(k) * c1(k)$$

$$xii(1) = ximin$$

$$xii(2) = ximax$$

7 Do 60 NX =1,2

$$xiinx = xii(nx)$$

C Effective diffusivity of HO2- ions in diaphragm is given
 C by DdHO2(k) (m2/s)

$$DdHO2(k) = di1(k) * 2.d0 * ed / (3.d0 - ed)$$

C Effective diffusivity of OH- ions in diaphragm is given
 C by DdOH(k) (m2/s)

$$DdOH(k) = di2(k) * 2.d0 * ed / (3.d0 - ed)$$

$$dphi = xiinx / xkapd(k)$$

$$cr1 = (0.d0 - c1(k)) / td$$

$$cr2 = DdHO2(k) * c1(k) * FAR * dphi / (R * t(k))$$

C xi1(k) is the current for perhydroxyl reaction (2.10)
 C on the anode
 C xi2(k) is the current for hydroxyl reaction (2.11)
 C on the anode

$$xi1(k) = -1000.d0 * FAR * (DdHO2(k) + ded) * (cr1 - cr2)$$

$$xi2(k) = xiinx - xi1(k)$$

If(xi2(k).lt.0.d0) xi2(k)= 1.d0

$$cr3 = -0.001d0 * xi2(k) / FAR$$

$$cr4 = (DdOH(k) + ded) * c2(k) / td$$

$$cr5 = DdOH(k) * c2(k) * FAR * dphi / (2 * R * t(k))$$

$$c2(k) = cr3 + cr4 + cr5$$

$$c22k = (cr4 - cr5) / c2(k)$$

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C      c2a(k) is the conc. of the OH- at the anode

      c2a(k) = c2k/c22k

C      Equilirium anode potential is given by vra(k) (V)
      vra(k)=0.401d0-
+      (R*t(k)/(4.d0*FAR))*log((c2a(k)**4)/pO2(k)/101.d0)

C      Anode over-potential is given by xna(k) (V)
      xna(k) = 0.69d0 + 0.1d0*log(abs(xi2(k)))/2.3d0

C      Diaphragm potential drop is given by vd(k) (V)
      vd(k) = dphi*td

C      Electrolyte potential adjacent to diaphragm in the cathode
C      bed is given by vcf(k)

      vcf(k) = vr - (vra(k) + xna(k) + vd(k))
      vcfk = vcf(k)

C      Subroutine brent to solve voltage balance in cathode bed
C      using bisection method
      call brent(func,0.05d0,0.4d0,1,0.1,eps2,phis,IR2)

C      Boundary conditions for Poisson's equation

      YA(1) = vcfk

      YA(2) = phis(1)

      YA(3) = -xiinx/xkapb(k)

      YA(4) = 0.d0

C      Store the values in NP, N matrix for potential

C      vb for electrolyte and vs for electrode

      vb(1,k) = YA(1)
      vs(1,k) = YA(2)

      x(1) = 0.d0

      Do 20 L = 2,NP

```

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lm = l-1

x(l) = x(lm) + delx

epsn = eps/(n-1)

+ call desolv(FM,NE,X(lm),X(l),YA,epsn,HSTART,HMIN,
HMAX,YB,NFUN,FLAG)

If(flag.eq.0)then

write(1,*)'warning-unable to integrate beyond',x(l)

Endif

Do 10 J = 1,NE

YA(J) = YB(J)

10 continue

vb(l,k) = YB(1)

vs(l,k) = YB(2)

20 continue

C calculate potential at different points along the
C width of the cathode bed

Do 25 J = 1,NP

vc(j,k) = vs(j,k) -vb(j,k)

xja1 = xkk1*dexp(bb1*(vc(j,k) - vr1(k)))

xja2 = xkok(k) + xk1*dexp(bb1*(vc(j,k) -vr1(k)))

xj1(j,k) = xja1/xja2

XY = vc(j,k)

XY1 = vr1(k)

If (XY.gt.XY1) xj1(j,k) = 0

xjb1 = xkk2*dexp(bb2*(vc(j,k) -vr2(k)))

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```

xjb2 = xkHO2(k) + xk2*dexp(bb2*(vc(j,k) - vr2(k)))

xj2(j,k) = xjb1/xjb2

If(XY.gt.XY2)xj2(j,k) = 0

25      continue

C      Add the partial Faradaic currents across cathode bed

sig11 = 0.d0
sig12 = 0.d0
sig21 = 0.d0
sig22 = 0.d0

Do 30 j =2,NP-1,2

sig11 = sig11 + xj1(j,k)
sig12 = sig12 + xj2(j,k)

30      continue

Do 40 j =3,NP-2,2

sig21 = sig21 + xj1(j,k)
sig22 = sig22 + xj2(j,k)

40      continue

br1 = xj1(1,k) + xj1(NP,k) + 4*sig11 +2*sig21
xib1(k) = s*delx*br1/3.d0

br2 = xj2(1,k) +xj2(NP,k) + 4*sig12 +2*sig22
xib2(k) = s*delx*br2/3.d0

C      Total current transferred from electrolyte to cathode matrix
xibed = xib1(k) + xib2(k)

xiii(nx) = xibed

fx(nx) = xii(nx) - xiii(nx)

60      continue

ffx = fx(1)*fx(2)

```

Appendix C

```

If(ffx.lt.0.d0)go to 70

xii(2) = xii(1)

xii(1) = temp1

xii(1) = (xii(1) + xii(2))/2

go to 7

70      absii = abs((xii(2) - xii(1))/xii(1))

      If(absii.le.eps)go to 80

      temp1 = xii(1)

      xii(1) = (xii(1) + xii(2))/2

      go to 7

80      xi(k) = (xii(1) + xii(2))/2

C      calculation completed for one length increment

C      Reinitialize the input values for next k

C      Mass balance

C      Net current for perhydroxyl formation reaction ((2.3) - (2.4) -
(2.11))
      curr1 = xib1(k) - xib2(k) - xi1(k)
      c1(k+1) = c1(k) + 1.d-3*curr1*w*del/(2*FAR*xl/rol(k))

C      Net current for hydroxyl formation reaction ((2.3) + 3(2.4) -
C      2(2.11))
      curr2 = xib1(k) + 3.d0*xib2(k) - 2.d0*xi2(k)
      c2(k+1) = c2(k) + 1.d-3*curr2*w*del/(2*FAR*xl/rol(k))

      c3(k+1) = c3(k)

C      Net current for oxygen formation reaction ((2.10) + (2.11)/2 -
C      (2.3))
      curr3 = xi1(k) + xi2(k)/2.d0 - xib1(k)
      g(k+1) = g(k) + 0.032d0*curr3*w*del/(2*FAR)

C      Pressure drop calculation

```

Appendix C

```

p(k+1) = p(k) - delp(k)

xib1t = xib1t + w*del*xib1(k)
xib2t = xib2t + w*del*xib2(k)
xilt = xilt + w*del*xi1(k)
Ireactor = Ireactor + w*del*xi(k)

C      Heat balance
      if (k.gt.1) then
+      t(k+1) = t(k) + 0.001d0*(vr-0.5d0)*xi(k)*w*del/(xl*cl) -
+      1000*pH2O(k)/(p(k) - pH2O(k))*(242.85)*(g(k)/ 0.032)/(l *cl)
+      +1000*pH2O(k-1)/(p(k-1) - pH2O(k-1))*(242.85)*(g(k)/ 0.032)/(l *cl)
      else
+      t(k+1) = t(k) + 0.001d0*(vr-0.5d0)*xi(k)*w*del/(xl*cl) -
+      1000*pH2O(k)/(p(k) - pH2O(k))*(242.85)*(g(k)/ 0.032)/(l *cl)
      end

85      continue

C      current efficiency of peroxide generation is given by CE
90      CE = 1000*xl*c1(n)*2*FAR/(rol(n)*Ireactor)

C      Specific energy of peroxide generation is given by SE
      SE = 2*FAR*Vr/(34*3600*CE)
      Stop

      End

C      Main program ends

C
*****

```

Appendix C

Double Precision Function Func(FFF)

Implicit Double Precision(A-H,O-Z)

External FM

Integer Flag

DOUBLE PRECISION YA(4),YB(4),X(100)

common/Blk1/k,xkapb(100)

common/Blk2/Hstart,Hmin,Hmax,NE

common/Blk3/tb,eps,np,delx,vcfk,xiinx

YA(1) = vcfk

YA(2) = FFF

YA(3) = -xiinx/xkapb(k)

YA(4) = 0.d0

x(1) = 0.d0

DO 20 L = 2,NP

LM = L-1

X(L) = X(LM) + delx

epsn = eps/(np-1)

+ CALL DESOLV(FM(I,X,Y),NE,X(LM),X(L),YA,EPSN,HSTART,HMIN,
HMAX,YB,NFUN,FLAG)

If(flag.eq.0)then

write(1,*)'warning unable to integrate beyond',X(l)

endif

Do 10 j = 1,ne

Appendix C

YA(j) = YB(j)

10 continue

20 continue

 Func = Yb(2)

 Return

 End

C *****

Appendix C

Double Precision FUNCTION FM(I,X,Y)

Implicit Double Precision(A-H,O-Z)

common/Blk1/k,xkapb(100)

+ common/Blk4/xkk1,xkk2,bb1,bb2,xkok(100),xkHO2(100),
xk1,xk2,vr1(100),vr2(100),xkaps(100),s

DOUBLE PRECISION Y(4)

If((Y(2)-Y(1)).GT.0.d0)then

xja = 0.d0

xjb = 0.d0

Endif

+ xja=xkk1*dexp(bb1*(Y(2)-Y(1)-vr1(k)))/(xkok(k)
+xk1*dexp(bb1*(Y(2)-Y(1)-vr1(k))))

If((Y(2)-Y(1)).gt.vr1(k))xja = 0.d0

+ xja=xkk2*dexp(bb2*(Y(2)-Y(1)-vr2(k)))/(xkHO2(k)
+xk2*dexp(bb2*(Y(2)-Y(1)-vr2(k))))

If((Y(2) - Y(1)).gt.vr2(k))xjb = 0.d0

go to (10,20,30,40)I

10 FM = Y(3)
return

20 FM = Y(4)
return

30 FM = s*(xja +xjb)/xkapb(k)
return

40 FM = -s*(xja +xjb)/xkaps(k)
return

end

C *****

Appendix C

```
+      Subroutine Desolv(FM,N,A,B,YA,EPS,HSTART,HMIN,HMAX,  
      YB,NFUN,FLAG)  
  
      Implicit Double Precision(A-H,O-Z)  
  
      Dimension YA(N),YB(N),Yold(100),Ynew(100)  
  
      Integer flag  
  
      External FM  
  
      C      FM: differential equation to be integrated  
      C      N: no. of equations to be solved  
      C      A: lower limit of integration  
      C      B: upper limit of integration  
      C      YA: initial condition (array)  
      C      eps: convergence criterion  
      C      hstart: initial stepping value of variable x  
      C      hmin: minimum stepping value of x  
      C      hmax: max. stepping value of x  
      C      YB: solution of differential equation at B (array)  
      C      nfun : no. of functional evaluations  
  
      hold = hstart  
  
      x= a  
  
      Do 10 i = 1,n  
  
          yold(i) = ya(i)  
  
10      continue  
  
      nfun = 0  
  
20      nfun = nfun + 6*n  
  
      C      calling subroutin rkck to solve equations at the value  
      C      of x and calculate the max. of |y(5) -y(4)|  
  
      call rkck(FM,n,x,yold,hold,ynew,ydiff)  
  
      gamma = (eps*hold/(ydiff*(b-a)))**0.25d0  
  
      C      get new value of hnew  
  
      hnew = 0.8d0*gamma*hold
```

Appendix C

```
If(gamma.lt.1.d0)then
If (hnew.lt.hold/10)hnew = hold/10.D0
C      If Hnew is smaller than hmin, integration failed
      If (hnew.lt.hmin)then
          flag = 0
          b = x
          Do 30 i =1,n
              yb(i) = yold(i)
30      continue
          return
      endif
C      otherwise if hnew is greater than hmin but less than
C      0.8*hold update hold and new value of gamma
      hold = hnew
      go to 20
else
      If (hnew.gt.5.d0)hnew = 5.d0*hold
      If(hnew.gt.hmax)hnew = hmax
      If (x+hold.lt.b)then
          x= x + hold
          Do 40 I = i,n
              yold(i) = ynew(i)
40      continue
          go to 20
```

Appendix C

```

else
    flag = 1
    hstart = hnew
    hold = b-x
    nfun = nfun + 6*n
    call rkck(FM,n,x,yold,hold,ynew,ydiff)
    Do 50 i = 1,n
        yb(i) = ynew(i)
50      continue
    return
endif
endif
end
end
```

C

Appendix C

Subroutine rkck(FM,N,X,Y,H,Y1,YDIFF)

C FM : differential equation to be integrated
C N : no. of equations to be solved
C X : initial value of x
C Y : initial value of y(array)
C H : increment in x
C Y1 : value of Y at x + h
C YDIFF : max. difference in solutions using 4th and
C : and 5th order Runge-kutta Cash-Carp methos

Implicit Double Precision(A-H,O-Z)

DOUBLE PRECISION K1(4),K2(4),K3(4),K4(4),K5(4),K6(4)

DOUBLE PRECISION Y(N),Y1(N),Y2(4)

c21 = 1.d0/5.d0

c31 = 3.d0/10.d0

c32 = 3.d0/40.d0

c33 = 9.d0/40.d0

c41 = 3.d0/5.d0

c42 = 3.d0/10.d0

c43 = -9.d0/10.d0

c44 = 6.d0/5.d0

c52 = -11.d0/54.d0

c53 = 5.d0/2.d0

c54 = -70.d0/27.d0

c55 = 35.d0/27.d0

c61 = 7.d0/8.d0

c62 = 1631.d0/55296.d0

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c63 = 175.d0/512.d0

c64 = 575.d0/13824.d0

c65 = 44275.d0/110592.d0

c66 = 253.d0/4096.d0

c71 = 2825.d0/27648.d0

c72 = 18575.d0/48384.d0

c73 = 13525.d0/55926.d0

c74 = 277.d0/14336.d0

c75 = 1.d0/4.d0

c81 = 37.d0/378.d0

c82 = 250.d0/621.d0

c83 = 125.d0/594.d0

c84 = 512.d0/1771.d0

c91 = c71 - c81

c92 = c72 - c82

c93 = c73 - c83

c94 = c74

c95 = c75 - c84

ydiff = 0.d0

DO 10 I = 1,N

K1(I) = H*FM(I,X,Y)

Y2(I) = Y(I) + C21*K1(I)

10

CONTINUE

DO 20 I = 1,N

Appendix C

$K2(I) = H*FM(I,X+C21*H,Y2)$
 $Y1(I) = Y(I) + C32*K1(I) + C33*K2(I)$

20 CONTINUE

DO 30 I = 1,N

$K3(I) = H*FM(I,X+C31*H,Y1)$
 $Y2(I) = Y(I) + C42*K1(I) + C43*K2(I) + C44*K3(I)$

30 CONTINUE

DO 40 I = 1,N

$K4(I) = H*FM(I,X+C41*H,Y2)$
 $Y1(I) = Y(I) + C52*K1(I) + C53*K2(I) + C54*K3(I) + C55*K4(I)$

40 CONTINUE

DO 50 I = 1,N

$K5(I) = H*FM(I,X+H,Y1)$
 $Y2(I) = Y(I) + C62*K1(I) + C63*K2(I) + C64*K3(I) + C65*K4(I) + C66*K5(I)$

50 CONTINUE

DO 60 I = 1,N

$K6(I) = H*FM(I,X+C61*H,Y2)$
 $Y1(I) = Y(I) + C81*K1(I) + C82*K3(I) + C83*K4(I) + C84*K6(I)$

$DIFF = DABS(C91*K1(I) + C92*K3(I) + C93*K4(I) + C94*K5(I) + C95*K6(I))$

$YDIFF = DMAX1(YDIFF,DIFF)$

60 CONTINUE

RETURN

END

C

Appendix C

```
C      SUBROUTIN FOR CALCULATING ROOTS OF AN EQUATION
C      USING BRENT'S METHOD
C      IT USES INCREMENTAL SEARCH FOLLOWED BY BISECTION
C      METHOD AND ULTIMATELY POLISHES THE ROOT USING
C      BRENT'S METHOD
```

```
      SUBROUTINE BRENT(F,XI,XF,NR,DELX,EPS,R,IR)
```

```
C      F          :      FUNCTION FOR WHICH BRENT'S ROOT
C      XI          :      STARTING VALUE OF THE BRACKET
C      XF          :      ENDING VALUE OF THE BRACKET
C      NR          :      NUMBER OF ROOTS SOUGHT
C      DELX :      INCREMENT
C      EPS          :      ERROR CRITERION
C      R            :      ROOTS FOUND(ARRAY)
C      IR           :      NO. OF ROOTS FOUND
```

```
      EXTERNAL F
```

```
      DIMENSION R(NR)
```

```
      X1 = XI
```

```
      Y1 = F(X1)
```

```
      ISTART = 1
```

```
C      IFF THE LOWER LIMIT IS ONE OF THE ROOTS
```

```
      IF(Y1.EQ.0.D0) THEN
```

```
          R(1) = X1
```

```
          X1 = X1 + EPS
```

```
          Y1 = F(X1)
```

```
          ISTART = 2
```

```
      ENDIF
```

```
C      FIND VARIOUS ROOTS BY BRACKETING BETWEEN X1 & X3
```

```
      DO 60 I = ISTART,NR
```

Appendix C

```
10      K = 0
20      X3 = X1 + DELX

      IF(X3.GT.XF) THEN

          IR = I - 1

          RETURN

      ENDIF

      Y3 = F(X3)

C      IF THE UPPER LIMIT IS ONE OF THE ROOTS

          IF(Y3.EQ.0.) THEN

              R(I) = X3

              X1 = X3 + EPS

              Y1 = F(X1)

              GO TO 60

          END IF

C      IF A ROOT EXISTS IN THE LIMIT CHECK FOR IT

C      SET A NEW BRACKET

          IF(Y1*Y3.GT.0.D0) THEN

              X1 = X3

              Y1 = Y3

              GO TO 20

          ELSE

              ENDIF

C      IF A ROOT IS FOUND THEN DO BISECTION THREE TIMES
```


C AND CHECK FOR DISCONTINUITY EACH TIME

J = 1

40 X2 = (X1 + X3)/2.D0

Y2 = F(X2)

IF(Y2.EQ.0.D0) THEN

R(I) = X2

X1 = X2 + EPS

Y1 = F(X1)

GO TO 60

END IF

IF(J.EQ.4)THEN

Y1 = F(X1)

Y2 = F(X2)

Y3 = F(X3)

GO TO 50

ENDIF

IF(Y1*Y2.GT.0.D0) THEN

X1 = X2

Y1 = Y2

ELSE

X3 = X2

Y3 = Y2

ENDIF

Appendix C

DYNEW = ABS(Y3-Y1)

IF(K.EQ.1.AND.DYNEW.GT.DYOLD) THEN

X1 = X3

Y1 = Y3

GO TO 10

ELSE

DYOLD = DYNEW

K =1

ENDIF

J = J +1

GO TO 40

C IF DISCONTINUITY DOES NOT EXIST, POLISH THE
C ROOT USING BRENT'S ALGORITHM

50 RF = Y2/Y3

S = Y2/Y1

T = Y1/Y3

P = S*(T*(RF-T)*(X3-X2) - (1.D0-RF)*(X2 -X1))

Q = (RF -1.D0)*(S-1.D0)*(T-1.D0)

X4 = X2 + P/Q

Y4 = F(X4)

IF(Y4.EQ.0.D0)THEN

R(I) = X4

X1 = X4 + DELX

Y1 = F(X1)

Appendix C

```

        GO TO 60
    ENDIF

    IF(ABS((P/Q)/X4).GT.EPS)THEN

        IF(X4.LT.X2) THEN

            X3 = X2

            Y3 = Y2

        ELSE

            X1 = X2

            Y1 = Y2

        ENDIF

        X2 = X4

        Y2 = Y4

        GO TO 50

    ELSE

        R(I) = X4

        X1 = X4 + EPS

        Y1 = F(X1)

        GO TO 60

    ENDIF

60      CONTINUE

        IR = NR

        RETURN

    END
C      *****
```

APPENDIX D

Kirchoff's laws for current

There are two laws that are used to analyse electrical circuits:

- 1) Kirchoff's voltage law
- 2) Kirchoff's current law

Kirchoff's voltage law

In any electrical circuit (e.g. Figure D.1), the total voltage around a closed loop is zero. That is the voltage around the closed loop 1, 2 and the external loop ABCD in Figure D.1 is zero [Cutnell and Johnson, 1989].

Figure D.1 Electrical circuit

The net effect of the voltage balance for the circuit shown in Figure D.1 translates into the following equations:

For closed loop 1 in Figure D.1,

$$V_1 - I_1 R_1 + I_2 R_2 - V_2 = 0 \quad (\text{D-1})$$

$$V_2 - I_2 R_2 + I_3 R_3 - V_3 = 0 \quad (\text{D-2})$$

Kirchoff's current law

In any node of an electrical circuit as shown in Figure D.2, the net current flowing into the node is equal to the net current flowing out of the circuit.

Figure D.2 Electrical node

The current law translates into the following equation:

$$I_1 = I_2 + I_3 \quad (\text{D-3})$$

Equations D-1 to D-3 may be used to solve for currents I_1 , I_2 and I_3 .

APPENDIX E

Two-cell reactor model code in MATLAB

The code for modelling the two-cell reactor is developed using MATLAB and is given below.

% Peroxide.m

% This program models a two-cell bipolar reactor for hydrogen peroxide generation

global n aa ac1 ac2 ba bc1 bc2 kapbk kapsk kapdk kperfk kgrafoil kacontact jlim1k
jlim2k tb tperf td s vr vrc1k vrc2k vrak coeff1 coeff2 coeff3 pk perf

% Input data for modelling the two-cell reactor:

% 1-perhydroxyl, 2-hydroxyl, 3-Na, 4-O₂

% Liquid and gas heat capacities are given by cl and cg respectively (KJ/kg/K)

cl = 4;

cg = 0.9;

% Concentration c (kmol/m³)

% c1(k),c2(k),c3(k)& c4(k) are the concentrations of perhydroxyl ion, hydroxyl ion,
% Na⁺ and O₂ respectively

% c11(1) is the concentration of perhydroxyl at cell1 inlet

% c12(1) is the concentration of perhydroxyl at cell 2 inlet

% c21(1) is the concentration of hydroxyl at cell 1 inlet

% c22(1) is the concentration of hydroxyl at cell 2 inlet

c1(1) = 1e-6;

c2(1) = 1;

c3(1) = 1;

c11(1)= c1(1);

Appendix E

$$c_{12}(1) = c_1(1);$$

$$c_{21}(1) = c_2(1);$$

$$c_{22}(1) = c_2(1);$$

% ded = eddy diffusivity through diaphragm (m²/s)

% Eddy diffusivity is to account for the convective flow through the diaphragm.

$$ded = 0;$$

% Diffusion coefficient at infinite dilution (m²/s) (CRC handbook, 25 C)

% 1-perhydroxyl, 2-hydroxyl, 3-Na, 4-O₂

$$dif_1 = 1.5e-9;$$

$$dif_2 = 5.3e-9;$$

$$dif_3 = 1.3e-9;$$

$$dif_4 = 2.4e-9;$$

% Diameter of the graphite felt fibre, m

$$df = 2e-5;$$

% Porosity of compressed graphite felt or cathode bed porosity (eb)

$$eb = 0.9;$$

% Diaphragm porosity is given by ed

$$ed = 0.8;$$

% Porosity of uncompressed graphite felt is given by eo

$$eo = 0.95;$$

% F = Faraday const. (kC/kmol)

$$F = 96486;$$

% Gas fraction in the holes is given by fgas (dimensionless)

Appendix E

$f_{\text{gas}} = 0;$

% Oxygen flow rate is given by $g(k)$ (kg/s)

% $g1(1)$ is the oxygen flow rate in cell1 inlet

$g(1) = 1.7\text{e-}5;$

$g1(1) = g(1);$

% $g2(1)$ is the oxygen flow rate in cell2 inlet

$g2(1) = g(1);$

% Liquid flow rate per reactor is given by l (kg/s)

$l = 3.36\text{e-}4;$

% Reactor length is given by le (m)

$le = 0.12;$

% k = counter for length increment

% km = mass transfer coefficient (m/s)

% $k1, k2$ are the electrochemical rate constants for reactions (2.3) & (2.4) (m/s)

% reference Journal of Chem. Engg of Japan (vol.18 no. 4 pp 364-371)

$k1 = 5\text{e-}7;$

$k2 = 1.6\text{e-}9;$

% Conductivity of grafoil is given by k_{grafoil} , S/m

$k_{\text{grafoil}} = 1\text{e}4;$

% Area conductivity of contact between grafoil and graphite felt is given by

% k_{acontact} , S/m²

$k_{\text{acontact}} = 5000;$

% Number of length increments of the reactor is given by lin

Appendix E

lin = 21;

% Molecular weight of O₂ is given by mw (kg/kmol)

mw = 32;

% n = no. of equations to be solved (4m+ 1) equations, where m is an integer

n = 17;

% Reactor pressure is given by p(k) kPa

p(1) = 901;

% Fraction of holes in the anode plate is given by perf (dimensionless)

perf = 0.05;

% Gas constant is given by R (kJ/kmol K)

R = 8.314;

% Temperature is given by t(k) (K)

t(1) = 298;

% Thickness of cathode bed is given by tb (m)

tb = 3.2e-3;

te = tb;

% Diaphragm thickness is given by td (m)

td = 1.5e-4;

% Perforation thickness is given by tperf (m)

tperf = 1.6e-3;

% vb = potential of liquid, vs = potential of solid

Appendix E

% vc = electrode potential at the face of the cathode bed

% Reactor voltage is given by vr (V)

vr = 2.5;

% Width of the reactor is given by w (m)

w = 2.5e-2;

% Input data complete

% c2a is the hydroxyl concentration on the anode, kmol/m³

% initial c2a concentration is assumed to be the inlet concentration (c2) and

% subsequently the concentration at anode is calculated by the flux equation

% through the diaphragm using current i2 for OH⁻ ions and assuming that HO₂-

% reaching the anode reacts completely

c2a(1) = c2(1);

% The current flowing through the reactor is given by Ireactor (A)

% and is initially set to a zero value

Ireactor = 0;

The total current density in cell1 for perhydroxyl formation (2.3) is initially set to zero

i1HO2 = 0;

The total current density in cell1 for perhydroxyl reduction (2.3) is initially set to zero

i1OH = 0;

%

del = le/lin;

for k = 1:lin;

pk = p(k);

Appendix E

$$p_{H_2O}(k) = \exp(16.5362 - 3985.44/(t(k) - 38.9974));$$

$$p_{O_2}(k) = p(k) - p_{H_2O}(k);$$

% Liquid density is given by $\rho_l(k)$ (kg/m³)

$$\rho_l(k) = 1000 \cdot (1 + 0.04 \cdot c_3(k));$$

% Liquid viscosity is given by $\mu_l(k)$ (Pas)

$$\mu_l(k) = 0.001 \cdot (1 + 0.5 \cdot c_3(k)) \cdot 10^{(-10.73 + 1828/t(k) + 0.01966 \cdot t(k) - 1.466e-5 \cdot (t(k)^2))};$$

% Gas viscosity is given by $\mu_g(k)$

$$\mu_g(k) = 1e-6 \cdot (18.11 + 0.663 \cdot t(k) - 1.879e-4 \cdot (t(k)^2));$$

% Diffusion coefficient for the given electrolyte viscosity is given by

% $d_{i1}(k)$, $d_{i2}(k)$, $d_{i3}(k)$ & $d_{i4}(k)$ (m²/s) where

% 1-perhydroxyl, 2-hydroxyl, 3-Na, 4-O₂

$$d_{i1}(k) = dif_1 \cdot t(k) \cdot 1e-3 / (\mu_l(k) \cdot 298);$$

$$d_{i2}(k) = dif_2 \cdot t(k) \cdot 1e-3 / (\mu_l(k) \cdot 298);$$

$$d_{i3}(k) = dif_3 \cdot t(k) \cdot 1e-3 / (\mu_l(k) \cdot 298);$$

$$d_{i4}(k) = dif_4 \cdot t(k) \cdot 1e-3 / (\mu_l(k) \cdot 298);$$

% Henry's constant of O₂ in H₂O is given by H_o

$$H_o = \exp((0.046 \cdot T^2 + 203.35 \cdot T \log(T/298) - (299.378 + 0.092 \cdot T) \cdot (T - 298) - 20.591e3) / (8.3144 \cdot T))$$

% Henry's constant of O₂ in NaOH is given by H (Sechenov equation)

$$H = H_o / 1.59$$

% Since the gas flow $g(k)$ does not change appreciably along the reactor length it may
% be assumed that it is identical for both the cells at any section k

% O₂ concentration in NaOH solution assuming O₂ in liquid to be in
% equilibrium with gas

$$c_4(k) = p_{O_2}(k) / (H \cdot 101);$$

% Equivalent diameter of the graphite felt cathode is given by d_e (m)

$$d_e = 1.5 \cdot d_f;$$

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% Specific surface area of the cathode bed is given by s (m^2/m^3)

$$s = 4 \cdot (1 - \text{eb}) / \text{df};$$

% Press gradient (Pa/m) in the reactor is given by $\text{delp}(k)$

$$\text{delp}(k) = (l / (\text{tb} \cdot w)) \cdot (0.36 + 1.182 \cdot ((g(k) / l)^{0.618})^2);$$

% Liquid hold up in the reactor is given by $\text{hl}(k)$

$$\text{hl}(k) = 1 - 0.907 \cdot ((l / (\text{tb} \cdot w))^{-0.362}) \cdot ((g(k) / (\text{tb} \cdot w))^{0.301});$$

% Mass transfer coefficient for O_2 through NaOH in the reactor is given by $\text{ko}(k)$ (m/s)

$$\text{ko}(k) = 5.9 \cdot ((l / (\text{tb} \cdot w))^{0.372}) \cdot ((g(k) / (\text{tb} \cdot w))^{0.301}) / s;$$

% Mass transfer limited real current density for oxygen generation is given by

% $\text{jlim1}(k)$ (A/m^2)

$$\text{jlim1}(k) = 1000 \cdot 2 \cdot F \cdot \text{ko}(k) \cdot c_4(k);$$

$$\text{jlim1k} = \text{jlim1}(k);$$

% Approximate mass transfer coefficient of HO_2^- ions in the NaOH solution is given

% by $\text{kHO2}(k)$ (m/s)

$$\text{kHO2}(k) = \text{ko}(k) \cdot \text{di1}(k) / \text{di4}(k);$$

% Mass transfer limited real current density for HO_2^- ion reduction is given by

% $\text{jlim2}(k)$ (A/m^2)

$$\text{jlim2}(k) = 1000 \cdot 2 \cdot F \cdot \text{kHO2}(k) \cdot c_1(k);$$

$$\text{jlim2k} = \text{jlim2}(k);$$

% To calculate conductivities of electrolyte and diaphragm the following constants

% are defined

$$\text{fr1} = 1000 \cdot \text{di1}(k) \cdot c_1(k) \cdot (1^2) \cdot (F^2) / (R \cdot t(k));$$

$$\text{fr2} = 1000 \cdot \text{di2}(k) \cdot c_2(k) \cdot (1^2) \cdot (F^2) / (R \cdot t(k));$$

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$$fr3 = 1000 * di3(k) * c3(k) * (1^2) * (F^2) / (R * t(k));$$

% Electrolyte conductivity is given by kapl(k) (S/m)

$$kapl(k) = fr1 + fr2 + fr3;$$

% Diaphragm conductivity is given by kapd(k) (S/m)

$$kapd(k) = 2 * kapl(k) * ed / (3 - ed);$$

% Compressed graphite felt conductivity is given by kaps(k) (S/m)

$$kaps(k) = 10 + 2800 * (((1 - eb) / eo)^{1.55});$$

% Effective electrolyte conductivity in the graphite felt fibre is given by kapb(k) (S/m)

$$kapb(k) = 2 * kapl(k) * eb * hl(k) / (3 - eb * hl(k));$$

% Electrolyte conductivity in the perforation is given by kperf(k) (S/m)

$$kperf(k) = kapl(k);$$

$$kperf_k = kperf(k);$$

$$kapbk = kapb(k);$$

$$kapsk = kaps(k);$$

$$kapdk = kapd(k);$$

% Equilibrium voltage for reaction (2.3) is given by vrc1(k) (V)

$$vrc1(k) = -0.076 - (R * t(k) / (2 * F)) * \log((c1(k) * c2(k)) / (p(k) / 101));$$

$$vrc1k = vrc1(k);$$

% equilibrium voltage for reaction (2.4) is given by vrc2(k) (V)

$$vrc2(k) = 0.878 - (R * t(k) / (2 * F)) * \log((c2(k)^3) / c1(k));$$

$$vrc2k = vrc2(k);$$

% Tafel parameters for reaction (2.11) on the anode is given by aa and ba

$$aa = 0.3;$$

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$$ba = 0.1/2.303;$$

% the exchange current density for perhydroxyl formation reaction (2.3) is given by

% j01 (A/m2) and Tafel parameters given by ac1 and bc1

$$j01 = 1000*2*F*k1*c4(k)*\exp(-0.546*F*vrc1k/(R*t(k)));$$

$$ac1 = -R*t(k)*\log(j01)/(0.546*F);$$

$$bc1 = R*t(k)/(0.546*F);$$

% the exchange current density for perhydroxyl reduction reaction (2.4) is given by

% j02 (A/m2) and Tafel parameters given by ac2 and bc2

$$j02 = 1000*2*F*k2*c1(k)*\exp(-0.263*F*vrc2k/(R*t(k)));$$

$$ac2 = -R*t(k)*\log(j02)/(0.263*F);$$

$$bc2 = R*t(k)/(0.263*F);$$

%Anode potential is given by vra(k) V

$$vra(k) = 0.401 - (R*t(k)/(4*F))*\log((c2a(k))^4*p(k)/101);$$

$$vrak = vra(k);$$

% Effective diffusivity of HO₂⁻ ions in diaphragm is given by DdHO₂ (k) (m²/s)

$$DdHO2(k) = di1(k)*2*ed/(3-ed);$$

% Effective diffusivity of OH⁻ ions in diaphragm is given by DdOH(k) (m²/s)

$$DdOH(k) = di2(k)*2*ed/(3-ed);$$

% The program makes use of various function files developed to accomplish the task of

% solving a set of non-linear equations

% Initial guessed values of X (the different current densities j) are used and then the differential calculated to get the augmented coefficient matrix.dX

% The augmented coefficient matrix dX is then solved using Gauss-Jordan method

% (function : gaussj) to generate the solution vector.

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```
% While using the Newton's method, a function : coeff_nonlinear is used to
% generate the augmented Jacobian matrix for the set of non-linear equations.
% The non-linear equations for each node are developed using a function :
% f_nonlinearequation.

% List of important arguments used in the program :
% n      :      Number of equations to be solved
% X      :      Solution vector for the set of linear equations
% B      :      Augmented Jacobian matrix for the set of non-linear equations
% dx     :      Solution vector of the augmented Jacobian matrix
% Guessing values of current density for n unknowns in the circuit

if k>1
    clear X dX B
end
X(1) = 2000;

for i = 1:(n-1)/2

    X(2*i) = jlim1k - 0.01;

    X(2*i+1) = jlim2k -0.01;

end

X_lin=X;                                % Linear solution stored for output

% Predefinitions for Newton's method

tol=1e-5;                                % Accuracy tolerance
maxit=50;                                % Maximum number of iterations
```

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```
iter=0;                % Initializing the counter
maxdx=1e10;            % Initializing a higher value to convergence criteria
alpha=0.95;            % Value for under relaxation parameter

% Newton's iterative method
while iter<maxit & maxdx>tol
    iter=iter+1;
    maxdx=0;
    B = coeff_nonlinear(X);
    dx=gaussj(B);
    nn = 0;
    for mm = 1:(n-1)/2
        nn = nn + 2;
        while (X(nn)+ alpha*dx(nn)>= jlim1k | X(nn)+ alpha*dx(nn)<= 0)
            dx(nn) = 0.6*dx(nn);
        end
        while (X(nn+1)+ alpha*dx(nn+1)>= jlim2k | X(nn+1)+ alpha*dx(nn+1)<= 0)
            dx(nn+1) = 0.6*dx(nn+1);
        end
    end
    end

    X=X+(alpha*dx);
    maxdx=max(abs(dx));
end

if maxdx<=tol          % Newton's method converged
    fprintf('\n\n\n Successful solution to problem achieved in')
    fprintf(' %2.0f iterations\n\n\n',iter)
    i=1:n;
    result=[i;X];
```


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% ii is the total superficial current density, A/m2

$$ii(k) = X(1);$$

% i11 is the superficial current density for peroxide oxidation at anode1, A/m2

% i12 is the superficial current density for peroxide oxidation at anode2, A/m2

$$i11(k) = 1000 * (DdHO2(k) + ded) * (c11(k) - 0) * F / td + 1000 * DdHO2(k) * (F^2) * c11(k) * ii(k) / (kapd(k) * R * t(k));$$

$$i12(k) = 1000 * (DdHO2(k) + ded) * (c12(k) - 0) * F / td + 1000 * DdHO2(k) * (F^2) * c12(k) * ii(k) / (kapd(k) * R * t(k));$$

% i21(k) is the superficial current density for hydroxyl reaction at anode1, A/m2

% i22(k) is the superficial current density for hydroxyl reaction at anode2, A/m2

$$i21(k) = ii(k) - i11(k);$$

$$i22(k) = ii(k) - i12(k);$$

$$coef1 = 1000 * (DdOH(k) + ded) * F / td;$$

$$coef2 = DdOH(k) * (F^2) * ii(k) / (2 * kapd(k) * R * t(k));$$

% c2a is the concentration of hydroxyl at the anode, kmol/m3

$$c2a(k+1) = (i21(k) - (coef1 + coef2) * c2(k)) / (coef2 - coef1);$$

% ibed11 is the current due to HO2- ion generation in cell 1

% ibed21 is the current due to HO2- ion reduction to OH- ion in cell 1

% ibed12 is the current due to HO2- ion generation in cell 2

% ibed22 is the current due to HO2- ion reduction to OH- ion in cell 2

$$ibed11(k) = (s * tb / ((n-1)/4)) * X(2);$$

$$ibed21(k) = (s * tb / ((n-1)/4)) * X(3);$$

for kk = 4:2:(n-1)/2

$$ibed11(k) = ibed11(k) + (s * tb / ((n-1)/4)) * X(kk);$$

$$ibed21(k) = ibed21(k) + (s * tb / ((n-1)/4)) * X(kk+1);$$

end

$$ibed12(k) = (s * tb / ((n-1)/4)) * X((n-1)/2+2);$$

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```
ibed22(k) = (s*tb/((n-1)/4))*X((n-1)/2 +3);

for kk = ((n-1)/2+4):2:(n-1)
    ibed12(k) = ibed12(k) + (s*tb/((n-1)/4))*X(kk);
    ibed22(k) = ibed22(k) + (s*tb/((n-1)/4))*X(kk+1);
end

% curby(k) is the percent current bypass through the perforations
% for any length increment k
curby(k) = (ii(k) - ibed11(k) - ibed21(k))/(2*ii(k))

%c11 is the perhydroxyl concentration in reactor1, kmol/m3
%c12 is the perhydroxyl concentration in reactor2, kmol/m3

c11(k+1) = c11(k) + 1e-3*w*del*(ibed11(k)-ibed21(k)- i11(k))/(2*F*I/rol(k));
c12(k+1) = c12(k) + 1e-3*w*del*(ibed12(k)-ibed22(k)- i12(k))/(2*F*I/rol(k));
c1(k+1) = (c11(k+1) + c12(k+1))/2;

%c21 is the hydroxyl concentration in reactor1, kmol/m3
%c22 is the hydroxyl concentration in reactor2, kmol/m3

c21(k+1) = c21(k) + 1e-3*w*del*(ibed11(k) + 3*ibed21(k) - 2*i21(k))/(2*F*I/rol(k));
c22(k+1) = c22(k) + 1e-3*w*del*(ibed12(k) + 3*ibed22(k) - 2*i22(k))/(2*F*I/rol(k));
c2(k+1) = (c21(k+1) + c22(k+1))/2;

% Na ion concentration is a constant
c3(k+1) = c3(k);

% For cell1, it is assumed that O2 generated in cell 2 is disengaged and
% is added to cell1 to increase the flow in cell1
g1(k+1) = g1(k) - 0.032*(i12(k)/2 + i22(k)/2 - ibed11(k))*w*del/(2*F);
g2(k+1) = g2(k) - 0.032*(ibed12(k))*w*del/(2*F);
```

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% Since the gas (oxygen) flow in the two cells (1&2) are not much different one may
% average the flow to calculate the pressure drop in subsequent length elements

$$g(k+1) = (g1(k+1) + g2(k+1))/2;$$

$$p(k+1) = p(k) - \text{delp}(k);$$

if k>1

$$t(k+1) = t(k) + 0.001 * (vr-1) * ii(k) * w * \text{del} / (2 * l * cl) - 1000 * (pH2O(k) / (p(k) - pH2O(k))) * (-42.85) * (g(k+1) / mw) / (l * cl) + 1000 * (pH2O(k-1) / (p(k-1) - pH2O(k-1))) * (-42.85) * (g(k+1) / mw) / (l * cl);$$

else

$$t(k+1) = t(k) + 0.001 * (vr-1) * ii(k) * w * \text{del} / (2 * l * cl) - 1000 * (pH2O(k) / (p(k) - pH2O(k))) * (-42.85) * (g(k+1) / mw) / (l * cl);$$

end

% Calculating the potential at various points in the electrode and electrolyte phase
% potbfl is the potential of the electrolyte at the cathode face (adjacent to diaphragm)
% potsfl is the potential of the electrode matrix at the cathode face (adjacent to
% diaphragm)

$$\text{potbfl} = vr - v_{rak} - aa - ba * \log(X(1)) - X(1) * td / \text{kapdk};$$

$$\text{potb}(k,1) = \text{potbfl} - X(1) * tb / (\text{kapbk} * ((n-1)/4));$$

$$\text{pots}(k,1) = \text{potb}(k,1) - ac1 - bc1 * \log(X(2)) + bc1 * \log(1 - X(2)) / j_{lim1k} + v_{rc1k};$$

$$\text{potsfl} = \text{pots}(k,1);$$

$$j_{sum1} = X(2) + X(3);$$

$$\text{count1} = 2;$$

$$\text{for } i = 2 : (n-1)/4$$

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```

    potb(k,i) = potb(k,i-1) - X(1)*tb/(kapbk*((n-1)/4))+ jsum1*s*(tb/((n-1)/4))*(tb/((n-1)/4))/kapbk;
    pots(k,i) = pots(k,i-1) - jsum1*s*(tb/((n-1)/4))*(tb/((n-1)/4))/kapsk;
    count1 = count1 + 2;
    jsum1 = jsum1 + X(count1) + X(count1 + 1);
end

    potbf2 = potb(k,(n-1)/4) - (X(1)-(s*tb/((n-1)/4))*jsum1)*tperf/(perf*kperfk) -X(1)*td/kapdk;
    potb(k,((n-1)/4 + 1)) = potbf2 - X(1)*tb/(kapbk*((n-1)/4));
    pots(k,((n-1)/4 + 1))=potb(k,((n-1)/4 + 1))-ac1-bc1*log(X((n-1)/2+2))+bc1*log(1-X(((n-1)/2+2))/jlim1k)+vrc1k;
    potsf2 = pots(k,((n-1)/4 + 1));
    jsum2 = X((n-1)/2+2) + X((n-1)/2+3);
    count2 = (n-1)/2+2;

    for i = (n-1)/4 +2 : (n-1)/2
        potb(k,i) = potb(k,i-1) - X(1)*tb/(kapbk*((n-1)/4))+ jsum2*s*(tb/((n-1)/4))*(tb/((n-1)/4))/kapbk;
        pots(k,i) = pots(k,i-1) - jsum2*s*(tb/((n-1)/4))*(tb/((n-1)/4))/kapsk;
        count2 = count2 + 2;
        jsum2 = jsum2 + X(count2) + X(count2 + 1);
    end

    Ireactor = Ireactor + w*del*ii(1);
    I1HO2 = I1HO2 + w*del*ibed11(k);
    I1OH= I1OH+ w*del*ibed21(k);

else
    % Newton's method did not converge
    fprintf('\n Newtons method did not converge for solution of non-linear equations \n')
end
end
end

CE = 2*1000*F*(2*I/rol(lin))*c1(lin+1)/(2*Ireactor)
% The current bypass through the entire reactor is given by CB
CB = (Ireactor- I1HO2 - I1OH)/(2*Ireactor)

```

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% The specific energy for peroxide generation is given by SE (kWh/kg)

$$\text{S.E.} = 2 \cdot F \cdot v_r / (2 \cdot 3600 \cdot 34 \cdot \text{CE})$$

%*****

function [B,C]=coeff_nonlinear(X)

% coeff_nonlinear is a Matlab function file for generating

% augmented Jacobian matrix for a set of non-linear equations.

% Elements of the Jacobian matrix are calculated using finite

% differences method.

global n jlim1k jlim2k

%delx=1e-6*X;

for i=1:n

C(i,1)=-f_nonlineareqn(i,X);

for j=1:n

delx = 1e-6*X;

xtemp=X(j);

nn = 0;

for mm = 1:(n-1)/2

% n is odd

nn = nn +2;

while (X(nn)+ delx(nn)>= jlim1k | X(nn)+ delx(nn)<= 0)

delx(nn) = 0.65*delx(nn);

end

while (X(nn+1)+ delx(nn+1)>= jlim2k | X(nn+1)+ delx(nn+1)<= 0)

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```
        delx(nn+1) = 0.65*delx(nn+1);
    end
end
X(j)=X(j)+delx(j);
ftemp=f_nonlineareqn(i,X);
X(j)=xtemp;
B(i,j)=(ftemp+C(i,1))/delx(j);
end
end

%*****
```

function X=gaussj(A)

n=size(A,1);

m=n+1;

while m>1

 if m>2

 pivot=1;

 smax=0;

 for i=1:m-1

 maxraw(i)=A(i,1);

 for j=2:m-1

 a=abs(A(i,j));

 if a>maxraw(i)

 maxraw(i)=a;

 end

 end

 s(i)=abs(A(i,1)/maxraw(i));

 if s(i)>smax

 smax=s(i);

 pivot=i;

 end

 end

 if pivot~=1

 for k=1:m

 temp=A(pivot,k);

 A(pivot,k)=A(1,k);

 A(1,k)=temp;

 end

 end

end

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```
for j=2:m
    for i=2:n
        B(i-1,j-1)=A(i,j)-A(1,j)*A(i,1)/A(1,1);
    end
end

for j=2:m
    B(n,j-1)=A(1,j)/A(1,1);
end

m=m-1;

for j=1:m
    for i=1:n
        A(i,j)=B(i,j);
    end
end

end

for i=1:n
    result(i)=A(i,1);
end

X=result;

%*****
```


function [B,A]=coef_inverse(X)

```
% coeff_nonlinear is a Matlab function file for generating
% augmented Jacobian matrix for a set of non-linear equations.
% Elements of the Jacobian matrix are calculated using finite
% differences method.
global n jlim1k jlim2k
delx=1e-6*X;
for i=1:n
    A(i)=-f_nonlineareqn(i,X);
    for j=1:n
        delx = 1e-6*X;
        xtemp=X(j);
        nn = 0;
        for mm = 1:(n-1)/2
            % n is odd
            nn = nn +2;
            while (X(nn)+ delx(nn)>= jlim1k | X(nn)+ delx(nn)<= 0)
                delx(nn) = 0.9*delx(nn);
            end
            while (X(nn+1)+ delx(nn+1)>= jlim2k | X(nn+1)+ delx(nn+1)<= 0)
                delx(nn+1) = 0.9*delx(nn+1);
            end
        end
        X(j)=X(j)+delx(j);
        ftemp=f_nonlineareqn(i,X);
        X(j)=xtemp;
        B(i,j)=(ftemp+A(i))/delx(j);
    end
end
%*****
```

function f=f_nonlineareqn(i,j)

% f_nonlineareqn is a matlab function file which finds the value

% of non-linear function twocell.m

global n aa1 aa2 ac1 ac2 ba1 ba2 bc1 bc2 kapbk kapsk kapdk kperf kgrafoil kacontact

jlim1k jlim2k tb tperf td s vr vrc1k vrc2k vrak coeff1 coeff2 coeff3 perf

% aa1 ,ba1 are the Tafel parameters for anode for cell1

%aa2 ,ba2 are the Tafel parameters for anode for cell2 (bipolar electrode)

% ac1 ,bc1 are the Tafel parameters for HO₂⁻ formation at the cathode

% ac2 ,bc2 are the Tafel parameters for HO₂⁻ reduction(OH⁻ formation) at the cathode

if i <=(n-1)/4 -1

% There are n equations to be solved. So the cathode is broken into

% (n-1)/4-1 closed loops or circuits for each of the cathodes

jsig = j(2) + j(3);

if i >=2

for k = 2:i

jsig = jsig + j(2*k) + j(2*k+1);

end

end

f= bc1*log(j(2*(i+1)))- bc1*log(j(2*i))+ bc1*log(jlim1k -j(2*i))-bc1*log(jlim1k-
j(2*(i+1))) + j(1)*(tb/((n-1)/4))/kapbk -jsig*s*(tb/((n-1)/4))*(tb/((n-
1)/4))*(1/kapsk + 1/kapbk);

end

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if $i \geq (n-1)/4$ & $i \leq (n-1)/2 - 2$

$j_{total} = j((n-1)/2 + 2) + j((n-1)/2 + 3);$

for $k = (n-1)/4 + 1 : i$

$j_{total} = j_{total} + j(2*k+2) + j(2*k+3);$

end

$f = bc1 * \log(j(2*(i+2))) - bc1 * \log(j(2*(i+1))) - j_{total} * s * (tb/((n-1)/4)) * (tb/((n-1)/4)) * (1/kapsk + 1/kapbk) + bc1 * \log(jlim1k - j(2*(i+1))) - bc1 * \log(jlim1k - j(2*(i+2))) + j(1) * (tb/((n-1)/4)) / kapbk;$

end

if $i \geq (n-1)/2 - 1$ & $i \leq n-3$

$m = 2;$

for $k = (n-1)/2 : i$

$m = m + 2;$

end

$f = ac1 + bc1 * \log(j(m)) - bc1 * \log(1 - j(m)/jlim1k) - vrc1k - ac2 - bc2 * \log(j(m+1)) + bc2 * \log(1 - j(m+1)/jlim2k) + vrc2k;$

end

if $i == n-2$

$j_{sum4} = 0;$

for $k = 2 : (n-1)/2 + 1$

$j_{sum4} = j_{sum4} + j(k);$

end

$\%v_{contact1}$ is the voltage drop due to contact between grafoil and graphite felt at the bipolar electrode

```

vcontact1 = jsum4/kacontact;

%vgrafoil is the voltage drop due to grafoil
vgrafoil = jsum4*tperf/kgrafoil;
f = -(j(1) - jsum4*s*(tb/((n-1)/4)))*tperf/(kperfk*perf)+vcontact1 + vgrafoil + aa2
+ ba2*log(jsum4*s*tb/((1-perf)*((n-1)/4)))+ vrak - vrc1k + ac1 + bc1*log(j((n-
1)/2)) - bc1*log(1-j((n-1)/2)/jlim1k);
end

if i == n-1
    jsum = 0;

    for k = ((n-1)/2 + 2):n
        jsum = jsum + j(k);
    end
    f = j(1) - jsum*(s*tb)/((n-1)/4);
end

if i == n
    jsum1 = 0;
    term1 = 0;
    jsum2 = 0;
    jsum3 = 0;
    term3 = 0;
    count1 = 2;
    count3 = (n-1)/2 + 2;
    for k = 2 : (n-1)/4
        term1 = term1 + j(count1) + j(count1 + 1);
        jsum1 = jsum1 + term1;
        term3 = term3 + j(count3) + j(count3 + 1);
        jsum3 = jsum3 + term3;
    end
end

```

Appendix E

```
count1 = count1 + 2;
count3 = count3 + 2;

end

for k = 2:(n-1)/2 + 1
    jsum2 = jsum2 + j(k);
end

%vcontact2 is the voltage drop due to the contact between end cathode and graphite felt
vcontact2 = j(1)/kacontact;
f= vr - vrak - aa1 - ba1*log(j(1))-j(1)*td/kapdk -j(1)*tb/kapbk + jsum1*s*(tb/((n-
1)/4))*(tb/((n-1)/4))/kapbk - (j(1)-(s*tb/((n-1)/4))*jsum2)*tperf/(perf*kperfk) -
j(1)*td/kapdk -j(1)*tb/kapbk + jsum3*s*(tb/((n-1)/4))*(tb/((n-1)/4))/kapbk - ac1 -
bc1*log(j(n-1)) + bc1*log(1-j(n-1)/jlim1k) + vrc1k -vcontact2;

end

%*****
```

APPENDIX F

Factorial experimental technique

Factorial experimental design is not only a very useful technique for doing parametric study of experiments but also allows the reduction in the number of experiments to analyze the responses of the parameters on a particular variable, based on individual and synergistic effects.

The technique in general involves a study of the responses on a particular variable due to n_f factors and the experiments are carried out at low (-) and high (+) levels of these factors. The analysis of the experiments requires 2^{n_f} experiments to be done. Another few runs may be done at the centre point of the high (+) and low level (-) of all the factors combined that would help determine the possibility of any non linear system behaviour and to get the confidence interval a.k.a. replicates [Murphy, 1977].

The effects that are studied can be categorized as main, interaction and curvature.

F1. Main effect

The main effect is defined as the response change on the variable under study with the change in the level of the factor (i.e. low to high or vice versa). If the number of factorial experiments in a particular study is N_r and the variable under study is a_i then the main effect may be calculated from the following equation:

$$\text{Main effect of } a_i = \frac{\Sigma(\text{responses at high } a_i) - \Sigma(\text{responses at low } a_i)}{\left(\frac{N_r}{2}\right)} \quad (\text{F-1})$$

The confidence interval for the main effect is:

$$\frac{\pm t_s s_t}{\sqrt{\frac{N_r}{4}}} \quad (F-2)$$

where s_t is the response error estimate based on f_d degrees of freedom and t_s is the student's statistic with f_d degrees of freedom at the desired confidence level (e.g. 90, 95%, 99%) and N_r the total number of factorial runs.

F2. Interaction effect

The calculation for interaction involves the same procedure as that for main effect. The interaction effect is calculated as the average response difference between one half of the factorial runs and the other half. Or to rephrase, for a two factor experiment with factors A and B, the interaction effect AB is the average distance between the effect of A at the 'high' level of B and the effect of A at the 'low' level of B.

F3. Curvature effect

The curvature effect is estimated as the difference between the average of the centre point responses and the average of the factorial points. Therefore a strong curvature indicates a high degree of non-linearity in the system.

The confidence interval for the curvature effect is calculated as:

$$\pm t_s s_t \sqrt{\frac{1}{N_r} + \frac{1}{C_r}} \quad (F-3)$$

where C_r is the total number of centre point runs.

APPENDIX G

Factorial experimental results and error analysis

The results for the factorial experiments on the small two-cell reactor are shown in Tables G.1 to G.5 below:

Table G.1 2² Factorial runs on small two-cell reactor with 2% perforation coverage and 0.8 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.33	1.0	1.0	1.2	1.2	24	20	38.0	38.5	0.013	0.015	81.0	92.9
1.00	1.8	1.8	1.9	1.9	25	22	39.0	39.0	0.025	0.026	76.8	78.8
2.33	2.6	2.8	2.4	2.4	32	28	38.5	38.0	0.067	0.053	59.3	46.3
3.00	2.9	3.0	2.5	2.6	35	31	38.0	38.5	0.076	0.066	51.6	45.1
3.66	3.4	3.2	2.5	2.7	39	34	38.0	38.0	0.082	0.077	45.6	42.5
4.00	3.4	3.3	2.6	2.8	40	36	38.0	37.5	0.086	0.083	43.5	41.7
4.66	3.5	3.5	2.7	2.9	44	39	38.0	38.5	0.094	0.088	40.8	38.7
5.00	3.8	3.6	2.8	3.0	47	41	38.0	38.0	0.097	0.096	39.3	39.1

Table G.2 2² Factorial runs on small two-cell reactor with 2% perforation coverage and 1.6 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.33	1.0	1.1	1.3	1.2	24	24	38.5	38.0	0.015	0.016	89.7	94.7
1.00	1.6	2.3	1.9	1.5	26	26	38.5	38.0	0.035	0.033	72.2	66.2
2.33	2.2	2.7	2.3	2.1	30	31	37.5	38.5	0.077	0.050	65.9	44.2
3.00	2.5	2.7	2.5	2.6	34	34	37.5	38.0	0.093	0.062	62.3	42.0
3.66	2.6	2.9	2.6	2.8	36	37	38.5	38.0	0.103	0.074	57.9	41.1
4.00	2.7	3.0	2.7	2.9	38	38	38.0	38.0	0.110	0.080	55.7	40.5
4.66	2.9	3.3	3.0	3.2	41	42	38.5	37.5	0.125	0.086	55.0	37.0
5.00	3.0	3.4	3.1	3.4	44	45	38.0	37.5	0.130	0.085	52.9	34.2

Table G.3 2² Factorial runs on small two-cell reactor with 4% perforation coverage
and 0.8 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.33	1.1	1.0	1.3	1.1	24	22	39.0	39.0	0.012	0.012	72.1	75.2
1.00	1.0	1.1	1.6	1.6	27	24	38.0	39.5	0.030	0.025	60.1	51.9
2.33	2.8	2.8	2.4	2.2	32	30	37.0	38.5	0.046	0.047	38.6	41.6
3.00	3.1	3.1	2.5	2.3	35	32	38.5	39.0	0.052	0.060	35.7	41.8
3.66	3.2	3.3	2.8	2.4	38	35	37.0	38.0	0.064	0.073	34.6	40.6
4.00	3.2	3.4	2.8	2.5	41	37	37.0	38.0	0.071	0.080	35.2	40.7
4.66	3.4	3.5	3.0	2.6	44	40	36.0	38.5	0.082	0.090	33.9	39.8
5.00	3.5	3.6	3.1	2.6	45	42	39.0	39.0	0.083	0.097	34.4	40.5

Table G.4 2² Factorial runs on small two-cell reactor with 4% perforation coverage and 1.6 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.33	1.0	1.0	1.2	1.0	22	21	37.5	38.0	0.013	0.013	78.4	76.4
1.00	1.4	1.8	1.6	1.5	24	22	38.0	37.5	0.033	0.033	67.2	65.3
2.33	2.4	2.6	2.3	2.1	30	27	38.0	38.0	0.062	0.055	54.1	47.6
3.00	2.7	2.8	2.5	2.3	32	30	38.5	38.0	0.075	0.068	51.5	45.8
3.66	2.9	3.0	2.6	2.7	34	33	38.0	38.0	0.088	0.078	48.6	43.0
4.00	3.0	3.1	2.7	2.8	36	36	37.5	39.0	0.100	0.084	50.2	43.9
4.66	3.2	3.2	2.8	2.9	40	39	37.5	38.0	0.111	0.095	47.8	41.5
5.00	3.3	3.3	2.9	2.9	41	41	37.0	38.0	0.116	0.099	46.0	40.1

Table G.5a 2^2 Factorial runs on small two-cell reactor with 3% perforation coverage and 1.2 mm perforation diameter (centre point)

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.33	1.1	1.1	1.2	1.1	27	21	38	38	0.013	0.014	78.4	81.4
1.00	1.9	1.9	1.7	1.7	29	23	38	38	0.030	0.035	66.3	71.3
2.33	2.6	2.6	2.5	2.3	34	29	38	38	0.070	0.055	64.6	48.0
3.00	3.1	2.8	2.7	2.4	38	31	38	39	0.058	0.066	59.2	45.4
3.66	3.2	2.9	2.8	2.6	40	35	38	39	0.102	0.080	56.6	45.6
4.00	3.3	3.1	2.9	2.7	42	36	38	38	0.107	0.086	53.8	43.8
4.66	3.6	3.3	3.0	2.8	46	39	38	38	0.116	0.094	50.6	40.8
5.00	3.7	3.4	3.1	3.0	48	42	38	38	0.123	0.098	49.9	39.7

Table G.5b 2^2 Factorial runs on small two-cell reactor with 3% perforation coverage and 1.2 mm perforation diameter (centre point)

Current density kA/m ²	Voltage cell 1 (V)	Voltage cell 2 (V)	Temp. (°C)	NaOH flow (ml/min)	H ₂ O ₂ conc. (M)	Current efficiency %
	Run no. 3	Run no. 3	Run no. 3	Run no. 3	Run no. 3	Run no. 3
0.33	1.0	1.2	22	37	0.015	86.2
1.00	1.9	1.7	24	38	0.029	70.2
2.33	2.6	2.2	30	37	0.053	44.6
3.00	2.8	2.4	33	38	0.065	43.6
3.66	2.9	2.5	36	38	0.088	47.9
4.00	3.0	2.5	38	37	0.096	47.3
4.66	3.4	2.6	42	38	0.102	44.3
5.00	3.8	2.7	45	38	0.113	46.0

The experimental conditions in Tables G.1 to G.5 are:

- NaOH concentration: 1M
- NaOH flow rate: 35-50 ml/min ($5.8\text{e-}7 - 8.3\text{e-}7 \text{ m}^3 \text{ s}^{-1}$)
- Oxygen flow rate: 400 ml/min ($6.6\text{e-}6 \text{ m}^3 \text{ s}^{-1}$) (STP)
- Diaphragm: SCIMAT 700/20
- Pressure (reactor inlet/outlet): 900/875 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2-4 %
- Perforation diameter: 0.8-1.6 mm

The results for the factorial design experiments on the medium two-cell reactor are shown in Tables G.6 to G.10 below:

Table G.6 2² Factorial runs on medium two-cell reactor with 2% perforation coverage and 0.8 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no. 1	2	Run no. 1	2	Run no. 1	2	Run no. 1	2	Run no. 1	2	Run no. 1	2
0.50	1.3	1.2	1.4	1.3	21	22	80	96	0.038	0.036	51.8	58.9
1.00	1.7	1.5	2.0	1.9	25	24	80	95	0.080	0.066	49.2	51.9
1.50	2.1	1.7	2.3	2.4	30	29	86	94	0.119	0.094	51.8	48.0
2.00	2.3	1.9	2.5	2.8	37	34	86	95	0.161	0.108	51.6	42.0
2.50	2.3	2.1	2.7	3.1	43	39	86	94	0.200	0.128	52.8	38.9
3.00	2.5	2.1	3.0	3.3	49	44	86	92	0.235	0.153	51.2	37.4
3.50	2.8	3.3	3.0	3.4	55	51	85	92	0.263	0.164	49.3	35.3
4.00	2.9	3.4	3.3	3.7	63	55	86	92	0.270	0.174	44.3	31.7
4.50	3.2	3.5	3.5	3.8	71	62	87	92	0.289	0.188	41.7	31.0

Table G.7 2^2 Factorial runs on medium two-cell reactor with 2% perforation coverage and 1.6 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.50	1.1	1.3	1.3	1.4	21	23	90	98	0.035	0.031	51.2	46.9
1.00	1.5	1.5	1.6	1.8	24	25	93	100	0.070	0.060	53.4	48.0
1.50	1.8	1.8	1.9	2.1	28	30	91	87	0.106	0.105	51.8	47.6
2.00	2.1	2.1	2.1	2.4	32	35	92	87	0.146	0.145	54.3	49.0
2.50	2.3	2.2	2.3	2.5	39	42	90	87	0.179	0.184	50.2	51.5
3.00	2.5	2.4	2.4	2.8	43	47	91	86	0.202	0.219	49.6	49.6
3.50	2.6	2.6	2.7	2.9	49	53	90	87	0.232	0.245	47.6	48.6
4.00	2.7	2.7	2.8	3.1	55	59	91	87	0.244	0.265	44.2	45.6
4.50	3.0	3.0	3.1	3.2	62	65	88	90	0.250	0.272	39.8	43.8

Table G.8 2² Factorial runs on medium two-cell reactor with 4% perforation coverage and 0.8 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.50	1.3	1.2	1.2	1.4	19	21	90	91	0.038	0.034	54.3	50.9
1.00	2.0	1.8	1.6	1.5	24	24	95	87	0.071	0.069	53.1	49.0
1.50	2.2	2.1	1.9	1.8	28	28	93	87	0.100	0.099	49.9	46.2
2.00	2.1	2.2	2.3	2.1	33	33	94	87	0.131	0.128	48.4	44.0
2.50	2.4	2.5	2.5	2.4	38	38	96	88	0.174	0.160	51.0	43.0
3.00	2.5	2.6	2.9	2.9	44	45	94	87	0.195	0.196	47.8	44.1
3.50	2.6	2.7	3.1	3.1	50	51	94	87	0.195	0.204	40.3	39.1
4.00	2.7	2.8	3.3	3.2	56	56	94	87	0.198	0.205	36.4	35.0
4.50	3.0	3.0	3.4	3.3	62	63	94	87	0.190	0.199	31.1	30.1

Table G.9 2^2 Factorial runs on medium two-cell reactor with 4% perforation coverage and 1.6 mm perforation diameter

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.50	1.2	1.2	1.3	1.3	21	22	92	96	0.038	0.036	54.9	58.9
1.00	1.6	1.5	1.8	1.9	23	24	93	95	0.068	0.066	50.5	51.9
1.50	1.7	1.6	2.2	2.4	29	29	93	94	0.098	0.094	48.2	48.0
2.00	2.1	1.9	2.3	2.8	33	34	93	95	0.125	0.108	47.5	42.0
2.50	2.2	2.0	2.8	3.1	39	39	94	94	0.150	0.128	45.7	38.9
3.00	2.3	2.1	3.1	3.3	48	44	93	92	0.161	0.153	39.0	37.4
3.50	2.4	2.3	3.2	3.4	52	51	93	92	0.175	0.164	37.1	35.3
4.00	2.5	2.4	3.4	3.7	57	56	92	92	0.193	0.174	35.2	31.7
4.50	2.6	2.5	3.7	3.8	64	62	92	92	0.214	0.188	33.9	31.0

Table G.10a 2² Factorial runs on medium two-cell reactor with 3% perforation coverage and 1.2 mm perforation diameter (centre point)

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	1	2	1	2	1	2	1	2	1	2	1	2
0.50	1.3	1.3	1.3	1.3	23	21	84	84	0.035	0.038	48.7	52.8
1.00	1.8	1.6	1.7	1.8	25	24	84	87	0.064	0.072	46.0	52.3
1.50	2.1	1.9	2.0	2.2	29	29	85	91	0.088	0.104	39.0	49.6
2.00	2.2	2.1	2.1	2.5	36	33	86	91	0.115	0.136	37.5	48.6
2.50	2.3	2.2	2.2	3.0	41	40	85	88	0.128	0.150	34.3	41.5
3.00	2.5	2.4	2.4	3.1	45	46	86	89	0.150	0.172	34.5	37.9
3.50	2.7	2.4	2.6	3.3	51	52	85	91	0.164	0.205	32.0	40.7
4.00	2.7	2.5	2.8	3.4	56	57	86	88	0.188	0.208	32.6	36.0
4.50	2.9	2.7	3.0	3.6	62	65	86	92	0.209	0.214	32.4	32.7

Table G.10b 2² Factorial runs on medium two-cell reactor with 2% perforation coverage and 1.6 mm perforation diameter (centre point)

Current density kA/m ²	Voltage cell 1 (V)		Voltage cell 2 (V)		Temp. (°C)		NaOH flow (ml/min)		H ₂ O ₂ conc. (M)		Current efficiency %	
	Run no.		Run no.		Run no.		Run no.		Run no.		Run no.	
	3	3	3	3	3	3	3	3	3	3	3	3
0.50	1.3	1.3	1.3	1.3	22	22	84	84	0.037	0.037	51.7	51.7
1.00	1.8	1.8	1.7	1.7	24	24	85	85	0.070	0.070	50.1	50.1
1.50	2.1	2.1	2.0	2.0	28	28	85	85	0.109	0.109	49.0	49.0
2.00	2.2	2.2	2.1	2.1	33	33	85	85	0.145	0.145	47.8	47.8
2.50	2.3	2.3	2.3	2.3	40	40	84	84	0.150	0.150	40.1	40.1
3.00	2.5	2.5	2.4	2.4	45	45	85	85	0.161	0.161	37.2	37.2
3.50	2.7	2.7	2.6	2.6	51	51	85	85	0.169	0.169	39.5	39.5
4.00	2.8	2.8	2.7	2.7	55	55	85	85	0.197	0.197	34.5	34.5
4.50	3.0	3.0	2.9	2.9	62	62	85	85	0.208	0.208	32.6	32.6

The experimental conditions in Tables G.6 to G.10 are:

- NaOH concentration: 1M
- NaOH flow rate: 85-95 ml/min ($1.4\text{e-}6 - 1.6\text{e-}6 \text{ m}^3 \text{ s}^{-1}$)
- Oxygen flow rate: 600 ml/min ($1\text{e-}5 \text{ m}^3 \text{ s}^{-1}$)(STP)
- Diaphragm: SCIMAT 700/20
- Pressure (reactor inlet/outlet): 900/600 kPa (abs.)
- Anodes: Grafoil and nickel mesh (100)
- Perforation coverage: 2-4 %
- Perforation diameter: 0.8-1.6 mm
- Constricted cathode

Error Analysis

An analysis is done of the various factors that attribute to the errors in the current density, peroxide current efficiency and specific energy values.

Tables G.11 and G.12 summarize the errors that may arise due to the various factors on the small and the medium reactor respectively. The net % error in the figures of merit due to each individual factor for small and medium reactor is given in Tables G.13 and G.14 respectively.

Table G.11 % Error in small reactor

Measurement	Unit	Basis	Error	% error
Current	Ampere	3	± 0.1	± 3.3
Flow rate: liquid	ml/min	20	± 0.5	± 2.5
Flow rate: gas	ml/min	400	± 5	± 1.3
Voltage	V	3	± 0.15	± 5
H ₂ O ₂ conc.	M	4 ml	± 0.05 ml	± 2.5
Pressure	kPa	800	± 25	± 3.1
Temperature	°C	20	± 0.5	± 2.5
Area	m ²	32e-4	± 1 e-4	± 3.1

Table G.12 % Error in medium reactor

Measurement	Unit	Basis	Error	% error
Current	Ampere	10	± 0.1	± 1
Flow rate: liquid	ml/min	40	± 0.5	± 1.2
Flow rate: gas	ml/min	600	± 5	± 1.2
Voltage	V	3	± 0.15	± 5
H ₂ O ₂ conc.	M	4 ml	± 0.05 ml	± 2.5
Pressure	kPa	800	± 25	± 3.1
Temperature	°C	20	± 0.5	± 2.5
Area	m ²	200e-4	± 6 e-4	± 3

Table G.13 % Error in figures of merit for small reactor

Figure of merit	% error
Current density, kA m ⁻²	$\pm 3.3 \pm 3.1 = \pm 6.4$
Peroxide current efficiency, %	$\pm 3.3 \pm 2.5 \pm 2.5 = \pm 8.3$
Specific energy, kWh kg ⁻¹	$\pm 5 \pm 8.3 = \pm 13.3$

Table G.14 % Error in figures of merit for medium reactor

Figure of merit	% error
Current density, kA m^{-2}	$\pm 1 \pm 3 = \pm 4$
Peroxide current efficiency, %	$\pm 1 \pm 1.2 \pm 2.5 = \pm 4.7$
Specific energy, kWh kg^{-1}	$\pm 5 \pm 4.7 = \pm 9.7$

APPENDIX H

Auxiliary equipment cost for alkaline peroxide electrosynthesis

Following auxiliary equipments (cf. Figure 7.1) are employed in the alkaline peroxide electrosynthesis:

- 1) Sodium hydroxide (NaOH) solution feed tank
- 2) Pump
- 3) Two-stage Compressor
- 4) Gas-liquid separator
- 5) Cooler

The calculation procedure for the cost of auxiliary equipment are based on the cost projection given in Matche.com and design calculations in [Perry's, 1984].

Feed and storage tank

Feed and storage tanks are designed to hold fluid volumes for the specified flow rates, assuming a typical residence times of 1800s. The feed and product flow rate of $21 \text{ m}^3 \text{ h}^{-1}$ (cf. Chapter 7) provides a feed tank volume of $\sim 11 \text{ m}^3$. The height to diameter ratio of 3 for a horizontal orientation gives height of 5 m and diameter of 1.67 m.

The cost for an 11 m^3 (2500 gallons approx.) stainless steel flat bottom tank [www.matche.com] is USD 14300.

Pump

The capital cost of the reciprocating pump for a feed flow rate of $21 \text{ m}^3 \text{ h}^{-1}$ ($\sim 80 \text{ gpm}$) is USD 10400 [www.matche.com].

The shaft power $W_{s,p}$ is calculated from the following equation [Uhlrich, 1984]:

$$W_{s,p} = \frac{F_v \Delta P_{diff}}{\epsilon_p} \quad \text{Watt} \quad (H-1)$$

where F_v is the volumetric flow rate ($\text{m}^3 \text{s}^{-1}$), ΔP_{diff} the pressure differential (9 e5 N m^{-2}) and ϵ_p is the pump efficiency ($\sim 80\%$ including motor efficiency).

The shaft power required for a flow rate of $0.0583 \text{ m}^3 \text{s}^{-1}$ ($21 \text{ m}^3 \text{h}^{-1}$) is 6.5 kW.

Two-stage compressor

The oxygen gas is required to be compressed from a pressure of near atmospheric (100 kPa abs.) to a pressure of 1200 kPa abs. For a compression ratio > 4 the compressor has to be broken into stages to prevent heating and also minimise the shaft power to the compressor.

For the present study, the compressor is broken into two stages with a compression ratio of 3.46 in each stage. The ratio is based on the fact that minimum power is required when the three pressures for the two compressors are in geometric progression (i.e. the pressure at the exit of first compressor is the geometric mean of the inlet pressure to the first compressor (100 kPa abs.) and the outlet pressure of the second compressor (1200 kPa abs.)

The shaft power is calculated from the following equation [Timmerhaus and Flynn, 1989]:

$$W_{s,c} = \left(\frac{m_v R T_{in}}{\epsilon_c} \right) \left(\frac{\gamma}{\gamma - 1} \right) \left[\left(\frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad \text{Watt} \quad (H-2)$$

where m_v is the molar flow rate of oxygen (mol s^{-1}) including the oxygen recycle, R the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T_{in} the inlet oxygen temperature to the compressor (K), γ the ratio of specific heats (C_p/C_v), P_{out}/P_{in} the ratio of outlet to inlet pressure for the compressor and ϵ_c is the compressor efficiency (72-92%).

For the present work, T_{in} is 293 K, γ is 1.4 (O_2 is a diatomic gas), each of the two compressors employed have a P_{out}/P_{in} of 3.46 and the compressor efficiency is assumed to be equal to 82%. The shaft power $W_{s,c}$ calculated based for a feed flow of 2.13 mol s^{-1} (7.7 kmol h^{-1}) is equal to 12.6 hp for each compressor. The cost estimate for each of the two compressors is USD 4200 (reciprocating: 200 psig (1360 kPa gauge)) [www.matche.com].

Gas-liquid separator

Gas-liquid separator is provided to release the excess O_2 from the electrolyte stream. It is a vertical column with packing in the upper part (cf. Figure 7.1) to prevent entrained electrolyte to leave the separator with O_2 .

The column can be designed for an O_2 flow of $180 \text{ m}^3 \text{ h}^{-1}$ and an aspect ratio of 3. The separator can be sized using equations (H-3) and (H-4) [Walas, 1987].

$$v_{\text{gas}} = 0.0304 \left(\frac{\rho_L}{\rho_G} - 1 \right)^{0.5} \quad m \text{ s}^{-1} \quad (\text{H-3})$$

$$D_{\text{sep}} = \frac{F_{v\text{gas}}}{0.75 v_{\text{gas}}} \quad m \quad (\text{H-4})$$

where v_{gas} is the velocity of the gas (O_2) in the separator (m s^{-1}), ρ_L the electrolyte density (kg m^{-3}), ρ_G the gas (O_2) density (kg m^{-3}), $F_{v\text{gas}}$ the volumetric flow rate of O_2 ($\text{m}^3 \text{ s}^{-1}$) and D_{sep} the diameter of the gas-liquid separator (m).

The separator diameter based on equations (H-3) and (H-4) is 0.07m. The corresponding separator height, including 0.07 m of disengaging space both ahead and above the mesh pad is 0.35 m.

The cost of a stainless steel gas-liquid separator 3" (0.07m) diameter with 250 psi rating is USD 1700.

Cooler

To reduce the rate of peroxide decomposition by reaction (2.5), a cooler is provided at the outlet of the product stream. The alkaline product stream is quenched using cooling water in countercurrent flow and the design temperatures for the cooler are:

Process stream (alkaline peroxide) inlet/outlet temperature: 353/303 K

Cooling water inlet/outlet temperature: 288/298 K

The design equations are:

$$Q = 1000 F_v \rho_L c_l (T_{p,in} - T_{p,out}) = 1000 F_{v,c} \rho_L c_l (T_{c,out} - T_{c,in}) = U A_{ex} LMTD \quad \text{Watt} \quad (H-5)$$

where Q is the heat transferred from the process stream to the cooling water (Watt), F_v is the process stream flow rate ($\text{m}^3 \text{s}^{-1}$), $F_{v,c}$ is the cooling water flow rate ($\text{m}^3 \text{s}^{-1}$), ρ_L the electrolyte density (kg m^{-3}), c_l the heat capacity of electrolyte ($4.2 \text{ kJ kg}^{-1} \text{K}^{-1}$), $T_{p,in}$ the process stream inlet temperature, $T_{p,out}$ the process stream outlet temperature, A_{ex} is the heat transfer area for the heat exchanger (cooler) (m^2) and LMTD is the log mean temperature difference for the cooler (K) given by:

$$LMTD = \frac{\left(\frac{T_{p,in} - T_{c,out}}{T_{p,out} - T_{c,in}} \right)}{\ln \left(\frac{T_{p,in} - T_{c,out}}{T_{p,out} - T_{c,in}} \right)} \quad K \quad (H-6)$$

Based on the flow rate of $0.0583 \text{ m}^3 \text{s}^{-1}$ ($21 \text{ m}^3 \text{h}^{-1}$) and an overall heat transfer coefficient U of $1250 \text{ W m}^{-2} \text{K}^{-1}$ [Perry's, 1984] the heat transfer area A_{ex} is calculated from equations (H-5) and (H-6) as $\sim 32 \text{ m}^2$ and the cooling water required is $105 \text{ m}^3 \text{h}^{-1}$. The cost of a stainless steel shell and tube floating head heat exchanger with heat exchanger area of 32 m^2 ($\sim 350 \text{ ft}^2$) and 300 psi rating is USD 39400 [www.matche.com].