JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 457–462

An experimental study of a fixed bed chlor-alkali reactor

COLIN OLOMAN, JOHN RADCLIFFE

Department of Chemical Engineering, The University of British Columbia, Vancouver, BC, V6T 1W5, Canada

Received 11 July 1985

A 100 A continuous ‘flow-by’ chlor-alkali membrane reactor was constructed with both anode and cathode consisting of fixed beds of 0.6 to 1 mm diameter graphite particles. The reactor was operated over a range of conditions with and without co-current flow of air or oxygen to the cathode. With an anolyte of 5 M NaCl and catholyte 1.4–3 M NaOH the reactor produced sodium hydroxide and chlorine with $\geqslant 80\%$ efficiency at temperatures 28–100° C, absolute pressure 270–970 kPa and superficial current density up to 3.3 kA m^{-2}. For operation at 100° C and an average pressure of 870 kPa with no gas delivered to the cathode, the cell voltage increased linearly from 2.5 V at 0.3 kA m^{-2} (10 A) to 4.0 V at 3.3 kA m^{-2} (100 A). When oxygen was delivered to the cathode at 1 litre min^{-1} under 870 kPa average pressure, the corresonding cell voltages were 1.6 V at 0.3 kA m^{-2} to 3.4 V at 3.3 kA m^{-2}. In operation with air under the same conditions the cell voltage rose from 1.6 V at 0.3 kA m^{-2} to 3.1 V at 1.6 kA m^{-2}. The performance of the oxygen cathode deteriorated with lower pressure and temperature due to mass transfer constraints on the oxygen reaction in the fixed bed electrode.

Nomenclature

a	Tafel constant (V)
b	Tafel coefficient (V per decade)
E^0	standard electrode potential (V)
E^r	equilibrium electrode potential (V)
i	superficial current density (kA m^{-2})
j	interfacial current density (kA m^{-2})
j_L	mass transfer limited interfacial current density (kA m^{-2})
P	partial pressure (kPa)
r'	effective resistivity (Ω m^{-2})
ΔV	difference in operating cell voltage (V)
Greek symbols	
η	overpotential (V)
Subscripts	
1	reaction 1
2	reaction 2

1. Introduction

The use of fixed bed electrodes in brine electrolysis has been described in several patents issued since about 1979 [1–3]. Although it is an unconventional concept there are several reasons for attempting to use fixed bed electrodes in chlor-alkali reactors.

According to De Nora and Pellegri [1], a fixed bed cathode in membrane chlor-alkali cells promotes uniform current density over the membrane area, thus avoiding mechanical and electrical stresses which damage the membranes of conventional commercial cells. The fixed bed design also relieves the mechanical problem of maintaining uniform electrode spacing and compresses the membrane against a perforated anode to give a ‘zero gap’ cell.

Fixed beds can replace gas diffusion electrodes as oxygen cathodes in chlor-alkali cells. McIntyre and Phillips [2] and Johnson and Chamberlain [3] have used fixed bed cathodes with oxygen gas dispersed in the caustic catholyte and demonstrated substantial reductions in cell voltage (over the ungassed case) for superficial current densities up to 1 kA m^{-2}. According to

0021-891X/86 $03.00 + .12

these authors the fixed bed cathode avoids problems of electrode flooding and delamination which would compromise the operation of gas diffusion electrodes in commercial chlor-alkali reactors.

Fixed beds may be used as anodes in chlor-alkali reactors [4]. Here there is the possibility that such anodes be made of relatively cheap granulated materials such as graphite or magnetite. Since the real current density on the particles is low these materials may suffer tolerable rates of erosion. It is also conceivable to use fixed beds as gas depolarized anodes, for example with hydrogen or sulphur dioxide reactant gases.

Cells employing fixed-bed electrodes are well suited to reactions that use or generate gases [5, 6]. Gas moves through the bed and electrolyte wets the electrode particles to provide conduction and electrode reaction in the matrix while the electrode remains in contact with the separator. In this way fixed bed electrodes can handle gas to liquid volumetric flow ratios of at least 10 with little change in cell resistance. Such a system also provides effective mass transfer for poorly soluble reactant gases [5, 7].

In view of the above features, fixed bed electrodes deserve further examination for chlor-alkali application. The work reported here is an experimental study of a membrane chlor-alkali cell with a fixed bed anode and a fixed bed oxygen depolarized cathode.

2. Experimental apparatus and procedures

This work was caried out with the bench scale continuous 'flow-by' single cell electrochemical reactor described in Fig. 1. The reactor consisted of an anode bed, a cation membrane and a cathode bed sandwiched between flat feeder electrode plates. The dimensions of each bed were: length 1 m, width 30 mm and thickness (in direction of current) 3 mm. The anode bed consisted of irregular graphite particles (UCAR of Union Carbide Corp., USA) in the size range 0.6 to 1.0 mm, while the cathode bed was of similar particles which had been pretreated by immersion in 0.4 M $AgNO_3$ and then heated to 600° C for 2 h. The membrane was 'Nafion' 214 (Dupont, USA), the anode feeder electrode was a plate (3 mm thick) of platinized titanium (Marston Ltd, UK) and the cathode feeder a plate (3 mm thick) of 316 stainless steel. Electrode beds were contained in 'Durabla' neoprene

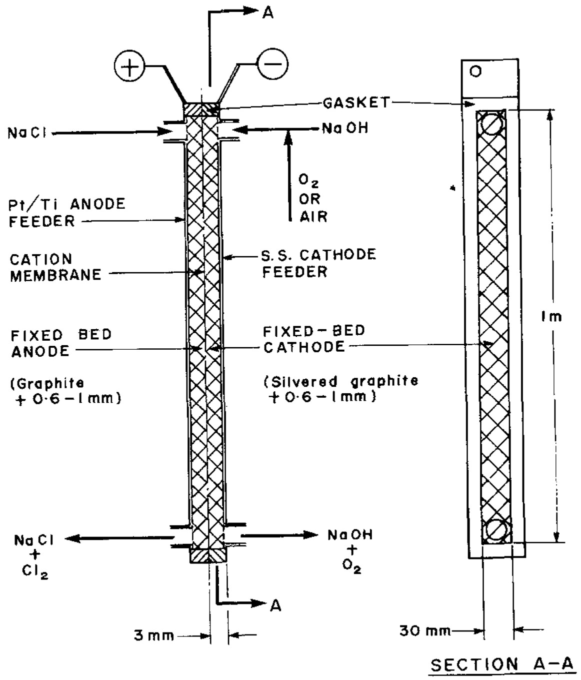

Fig. 1. Detail of experimental fixed bed chlor-alkali reactor.

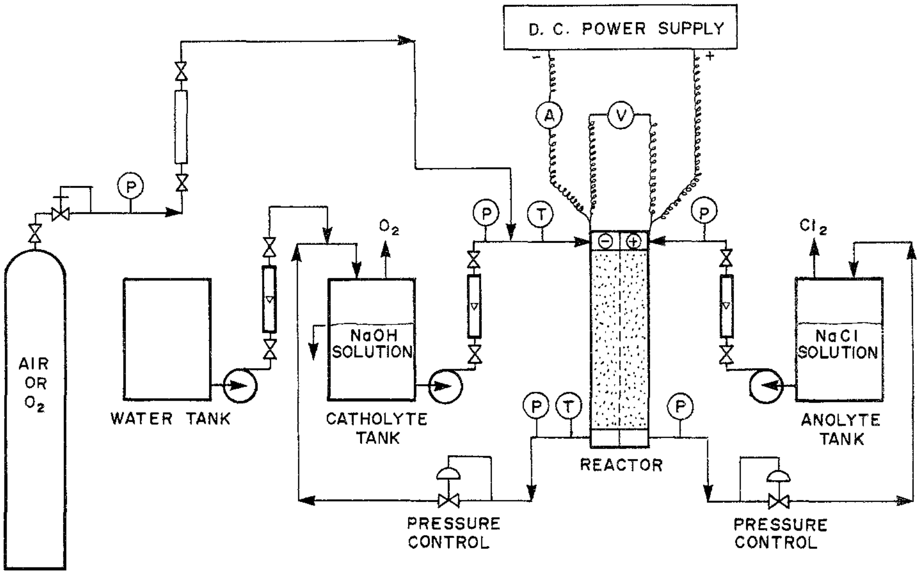

Fig. 2. Flow diagram of apparatus used with the fixed bed chlor-alkali reactor.

impregnated asbestos gaskets (3 mm thick), the feeder plates were fitted with $\frac{1}{8}$ inch NPT inlet and outlet ports and the reactor was sealed to an internal pressure of 1000 kPa by compression between bolted steel channels (not shown). The assembled reactor was wrapped with heating tape and fibreglass insulation and installed in the test bed shown in Fig. 2.

In operation, metered flows of anolyte and catholyte were recycled through the respective electrode chambers and air or oxygen was metered to a tee in the catholyte feed line. A d.c. power supply delivered up to 100 A/10 V and the concentration of sodium hydroxide in the catholyte was adjusted by a controlled flow of water to the catholyte tank. Catholyte outlet temperature from the reactor was controlled up to 100° C by manual adjustment of power to the heating tape, and pressure in both cathode and anode chambers was maintained up to 1000 kPa* by pressure controls on both fluid outlets. The anolyte was a 5 M solution of laboratory grade sodium chloride and the catholyte was a solution of laboratory grade sodium hydroxide, both in deionized water. Gases were compressed air or oxygen of $\geqslant 99\%$ purity.

Experimental runs of about 30 min duration each were carried out over a range of conditions to examine the effect of several variables on reactor performance. The major independent variables were the current to the reactor (2–100 A), the composition and flow of gas to the cathode (air or O_2 from 0 to 34 $cm^3 s^{-1}$ STP), concentration of sodium hydroxide in the catholyte feed (1.4–10 M), reactor outlet pressure (0–700 kPa) and catholyte outlet temperature (20–100° C). For runs at high temperature the anolyte was preheated to about 70° C by recycling through the heated cell for about 2 h prior to the run. Anolyte and catholyte flows were maintained at 0.5 to 1 $cm^3 s^{-1}$ and 0.5 $cm^3 s^{-1}$, respectively.

The current efficiency for sodium hydroxide was determined in some runs by titrating samples of the feed and product catholyte with 2 N H_2SO_4 solution. Checks for peroxide in the catholyte product were made by titrating an acidified sample with 0.01 N potassium permanganate solution. Chlorine and oxygen contents of the anode product gas were measured in some runs by absorption into a solution of potassium hydroxide followed by potassium pyrogallate. No attempt was made to determine the current efficiency for hydrogen.

---

* All pressures are absolute.

3. Results

The fixed bed reactor operated smoothly to produce sodium hydroxide and chlorine. The current efficiency for sodium hydroxide varied from about 100% at 50 A to 80% at 100 A. With the cell operating at 80 A, 90° C and 770 kPa outlet pressure, the current efficiencies for chlorine and oxygen at the anode were about 90% and 10%, respectively.

Preliminary tests with air and oxygen flow to the cathode were carried out at outlet conditions of 28° C and 100 kPa, with 3 M NaOH in the catholyte feed. The results in Fig. 3 show that the gas flow decreases reactor voltage at superficial current densities below about 1.6 kA m^{-2}. Increasing the air or oxygen flow from 17 to 34 cm^3 s^{-1} STP caused the voltage to change about ± 1% over the conditions of Fig. 3.

Fig. 4 shows the results of running the tests of Fig. 3 with 70° C and 100 kPa outlet conditions. The higher temperature reduces cell resistance but makes little change to the relative effects of air and oxygen on the reactor voltage. Fig. 4 also demonstrates that increasing the concentration of sodium hydroxide in the catholyte feed from 3 to 10 M suppresses the effect of oxygen on reactor voltage so that oxygen flow gives no reduction of reactor voltage above a superficial current density of 0.6 kA m^{-2}. A small decrease in voltage was realized by changing the flow of both electrolytes from downwards to upward. No peroxide (< 0.001 M) was detected in the analysis of samples of catholyte product from several runs with oxygen flow at 34 cm^3 s^{-1}, 3 M NaOH at 70° C and currents from 10 to 50 A.

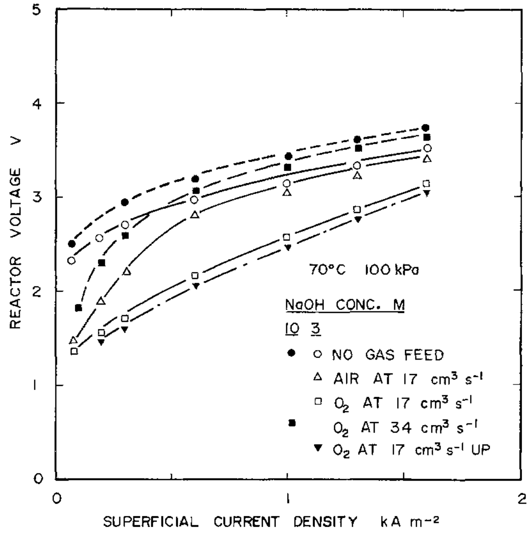

Fig. 4. Effect of air and oxygen flow on reactor voltage at 70° C and 100 kPa. – – –, downward flow; ——–, upward flow. Catholyte (——): 3 M NaOH, 0.5 cm^3 s^{-1}, 24–70° C; catholyte (– – –): 10 M NaOH, 0.5 cm^3 s^{-1}, 24–80° C. Anolyte: 5 M NaCl, 0.7 cm^3 s^{-1}, 70–80° C. Anode pressure: 370 kPa (in), 100 kPa (out). Cathode pressure ●, ○, 370 kPa (in), 100 kPa (out); △, 430 kPa (in), 100 kPa (out); ▼, □, 400 kPa (in), 100 kPa (out); ■, 430 kPa (in), 100 kPa (out).

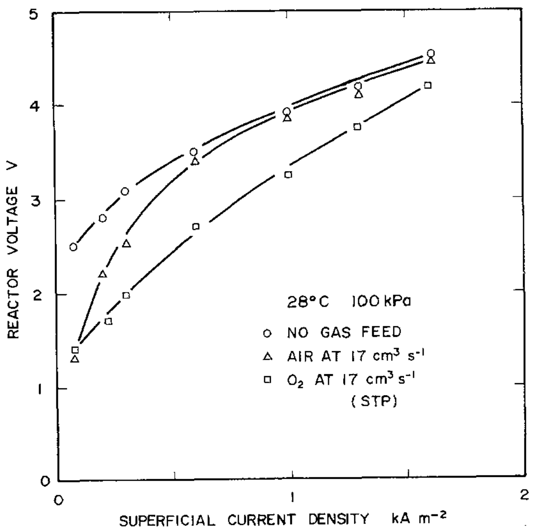

Fig. 3. Effect of air and oxygen flow on reactor voltage at 28° C and 100 kPa. Downward flow. Catholyte, 3 M NaOH at 0.58 cm^3 s^{-1}; anolyte, 5 M NaCl at 0.7 cm^3 s^{-1}. Temperature: 22° C (in), 28° C (out). Anode pressure: 290 kPa (in), 100 kPa (out). Cathode pressure: ○, 370 kPa (in), 100 kPa (out); △, 400 kPa (in), 100 kPa (out); □, 400 kPa (in), 100 kPa (out).

In a final set of runs the outlet pressure from both electrode chambers was controlled to 770 kPa and temperature increased to 100° C. The catholyte feed concentration was also dropped to 1.4 M and flows were directed upwards through the cell. The results in Fig. 5 show considerable improvement in reactor operation over Figs 3 and 4 with respect to voltage requirements (note the changed scale of the abscissa). Air flow gave significant voltage reduction up to 1.6 kA m^{-2} while oxygen flow lowered the voltage by 0.85 V at 0.3 kA m^{-2} to 0.6 V at 3 kA m^{-2}, i.e. below the values obtained without gas feed to the cathode.

4. Discussion

The interest of this work centres on the reduction of reactor voltage and possible energy savings achieved by operation of the fixed-bed cathode with a co-current flow of gas containing oxygen [8, 9].

In principle, the effect of oxygen on reactor voltage is known to be due to the difference in equilibrium cathode potential from Reaction 1 to Reaction 2.

$$2H_2O + 2e \rightleftharpoons H_2 + 2OH^- \qquad (1)$$

$$E^0 = -0.828 \text{ versus SHE}$$

$$2H_2O + O_2 + 4e \rightleftharpoons 4OH^- \qquad (2)$$

$$E^0 = +0.401 \text{ versus SHE}$$

Of course, the full 1.23 V potential gap is not obtained under operating conditions. The reactor voltage reduction depends, then, on the overpotential of the oxygen electrode and the effective resistance of the catholyte. Other things being equal, for a given cell with and without an oxygen supply to the cathode, the difference in operating voltage may be expressed as

$$\Delta V \simeq E_1^r - E_2^r + (\eta_1 - \eta_2) + i(r_2' - r_1') \qquad (3)$$

where the overpotentials have negative values approximated from the Tafel relations.

$$\eta_1 = a_1 + b_1 \ln j_1 \qquad (4)$$

$$\eta_2 = a_2 + b_2 \ln j_2 + b_2 \ln ((j_L - j_2)/j_L) \qquad (5)$$

In a three-dimensional flow-by cathode the reactant concentration, superficial current density in the electrolyte and the current density at the cathode surface change through the electrode [10]. For the purpose of this discussion, Equation 3 can be considered to apply to average conditions over the cathode volume.

The effect of oxygen pressure on the difference in equilibrium potential between Reactions 1 and 2 is summarized in the relation

$$E_1^r - E_2^r = -1.23 - 0.0295 \log(p_{H_2} p_{O_2}^{1/2}) \quad \text{at } 25°\text{C} \qquad (4)$$

Under the conditions of Fig. 3 this difference is 1.233 and 1.244 V, respectively, for depolarization by air and by oxygen. At the higher pressure of Fig. 5, the corresponding values are about 1.26 and 1.29 V plus a small correction for the effect of temperature on the equilibrium potentials. In Figs 3, 4 and 5 the equilibrium potential gap is approached at zero current with depolarization by both air and oxygen.

The effective resistance of the electrolyte increases with gas flow through the cathode due to the corresponding drop in liquid hold-up [5]. However, the slope of the lines in Figs 3, 4 and 5 indicate that the increased resistance is largely compensated by small overpotentials for the oxygen process at low current density. The potential gap decreases with rising superficial current density due to mass transport constraints on the oxygen reaction. Oxygen transport constraints are most severe with air as the depolarizing gas, due to the low partial pressure of oxygen and added resistance to mass transfer in the gas phase. There also appears to be a problem associated with high caustic concentration in the catholyte (Fig. 4), possibly a result of the high viscosity and decreased oxygen solubility in this solution.

The improvement in performance of the depolarized cathode from Figs 3 to 4 to 5 is

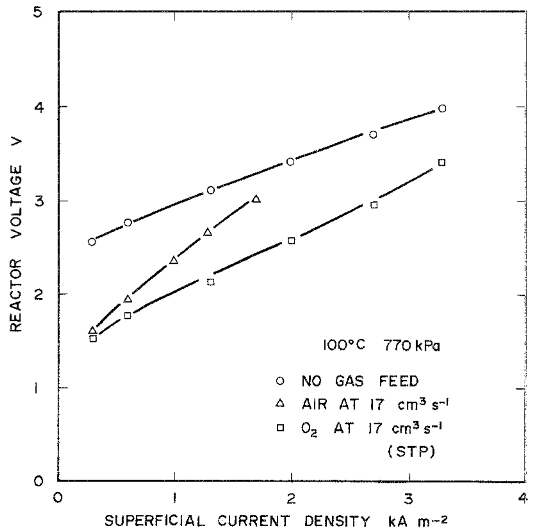

Fig. 5. Effect of air and oxygen flow on reactor voltage at 100° C and 770 kPa. Upward flow. Catholyte: 1.4 M NaOH, 0.5 cm^3 s^{-1}, 24–100° C. Anolyte: 5 M NaCl, 0.5 cm^3 s^{-1}, 70–100° C. Anode pressure: 970 kPa (in), 770 kPa (out). Cathode pressure: 970 kPa (in), 770 kPa (out).

largely due to improved oxygen transfer resulting from increased temperature, decreased caustic concentration and increased oxygen pressure. Between Figs 4 and 5, for the respective cases of air and oxygen as the depolarizing gas, the average oxygen pressure in the cathode rises from 50 to 170 kPa and from 250 to 870 kPa. The corresponding three-fold increase in oxygen transfer limited current density is the major cause of improved cathode performance.

At $3\,\mathrm{kA\,m^{-2}}$ and a current efficiency of 95% under the conditions of Fig. 5, the saving of electrochemical energy for an oxygen depolarized chlor-alkali cell would be about $0.9\,\mathrm{kW\,h\,kg^{-1}}$ NaOH. In this case the energy required for pumping and gas compression is about $0.8\,\mathrm{kW\,h\,kg^{-1}}$ NaOH. However, the mechanical energy consumption may be significantly reduced by using cathode materials with high specific surface, such as carbon fibres or granules of carbon black in Teflon [11], which would allow operation at lower pressure or reduced gas load. There are also savings in energy for chlorine drying and compression from operating a chlor-alkali reactor at superatmospheric pressure.

5. Conclusions

This work demonstrates the use of fixed bed electrodes as both anode and cathode in a chlor-alkali membrane reactor operated at superatmospheric pressure. Fixed bed electrodes performed well in a laboratory cell for short term tests up to a superficial current density of $3.3\,\mathrm{kA\,m^{-2}}$ and pressure of 970 kPa. When operated in the 'trickle-bed' mode at an average pressure of 870 kPa, the fixed bed cathode was effectively depolarized by oxygen at a superficial current density up to $3.3\,\mathrm{kA\,m^{-2}}$. Mass transfer of oxygen was the major constraint on the performance of the fixed bed as an oxygen cathode in this work.

The fixed bed electrochemical chlor-alkali reactor is technically feasible and deserves consideration for industrial application.

Acknowledgement

This work was done in 1980 with financial support from the University of British Columbia and the National Research Council of Canada.

References

[1] O. De Nora and L. Pellegri, US Patent 4 177 116, December 4, 1979 (assigned to Oronzio De Nora Implanti Elettrochimica. Sp., Milan Italy).

[2] J. A. McIntyre and R. F. Phillips, US Patent 4 224 192, September 23, 1980, 4 317 704, March 2, 1982 (assigned to Dow Chemical Co., Midland, Michigan, USA).

[3] H. B. Johnson and R. D. Chamberlain, US Patent 4 244 793, January 13, 1981 (assigned to PPG Industries Inc., Pittsburgh, PA, USA).

[4] F. Goodridge and B. M. Ismail, Symp. Electrochem. Engineers, 1971, Inst. of Chemical Engineers, London, Symposium Series No. 37 (1973) p. 29.

[5] C. Oloman, *J. Electrochem. Soc.* **126** (1979) 1885.

[6] G. Kreysa. *Chem. Ing. Tech.* **55** (1983) 23.

[7] K. Takahashi and R. Alkire, *Chem. Eng. Commun.*, in press.

[8] E. Yeager, 'Electrochemistry in Industry' (Proc. Int. Symp.) (edited by U. Landau), Plenum, New York (1982) pp. 29–58.

[9] K. Kordesch, S. Jahangir and M. Schautz, *Electrochim. Acta* **29** (1984) 1589.

[10] R. Alkire and P. K. Ng, *J. Electrochem. Soc.* **121** (1974) 95.

[11] J. A. McIntyre and R. F. Phillips, 'Electrochemical Process and Plant Design' (Proc. Symp.), Vol. 83–6, (edited by R. Alkire *et al.*), Electrochemical Society, Pennington (1983) p. 79.