JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 437–443

The production of hypobromite and of propylene oxide in an electrochemical pump cell

J. GHOROGHCHIAN, R. E. W. JANSSON, D. JONES

Chemistry Department, The University, Southampton

Received 25 January 1977

Hypobromite and propylene oxide have been generated in an electrochemical pump cell and the production rates have been related to the space-time histories of the species within the cell. Production rates are typically 0·15 and 0·11 mol h^{-1} dm^{-2} (depending on current density) and energy yields 1·4 and 2·7 kW h kg^{-1} respectively. Other figures of merit are given.

Symbols

A electrode area
c concentration
D diffusion coefficient
F the Faraday
$G = h/r_o$ gap ratio
h interelectrode gap
n number of electrons transferred
$k_M = I/nFAc = D/\delta$ mass transfer coefficient
$(Re) = Q/h\nu$ channel Reynolds number
$(Re_L) = Q/\pi r\nu$ local Reynolds number
$(Re_\phi) = \omega r_o^2/\nu$ rotational Reynolds number
Q volumetric flow rate
r radius
r_o outer radius of disc electrode

Greek

δ Nernst diffusion layer thickness
ν kinematic viscosity
ω angular velocity

1. Introduction

A schematic diagram of a simple form of electrochemical pump cell [1] is shown in Fig. 1(a). One electrode rotates relative to another producing very high mass transfer rates ($k_M \simeq 0{\cdot}4$ cm s^{-1} in metal deposition) while pumping the solution radially outwards [2–5]. The measurement of the response evoked by a concentration pulse [6] has shown [7] that essentially the cell behaves as a plug flow reactor with respect to the radial flow, but that within each radially expanding annular fluid element the degree of anolyte/catholyte mixing is determined by the rotational motion. Thus the space-time histories of the reactants, as well as the mass transfer rate, are controlled by two Reynolds numbers:

(1) the channel Reynolds number, $(Re) = Q/h\nu$, which relates to the volumetric throughput and mean residence time in the cell; and
(2) the rotational Reynolds number, $(Re_\phi) = \omega r_o^2/\nu$, which has a dominating influence on the mixing during that residence time.

At zero rotational speed the cell is identical to the geometrically similar capillary gap cell [8] and another parameter becomes important:

(3) the local Reynolds number, $(Re_L) = Q/\pi r\nu$, which is a measure of the local environment of the flow at any radius r.

It has been shown [2, 9, 10] that there is a critical value of (Re_L) at which an initially turbulent flow re-laminarizes, which has an important effect on mass transfer and cross-gap mixing. However when one electrode is rotating (Re_ϕ) becomes controlling and (Re_L) is unimportant.

The pump cell, therefore, is particularly suitable for reactions which proceed via the mixing of electrogenerated species; its application to two such reactions is reported here, the formation of hypobromite by the electrolysis of sodium bromide and the epoxydation of propylene, to which the first reaction is a precursor.

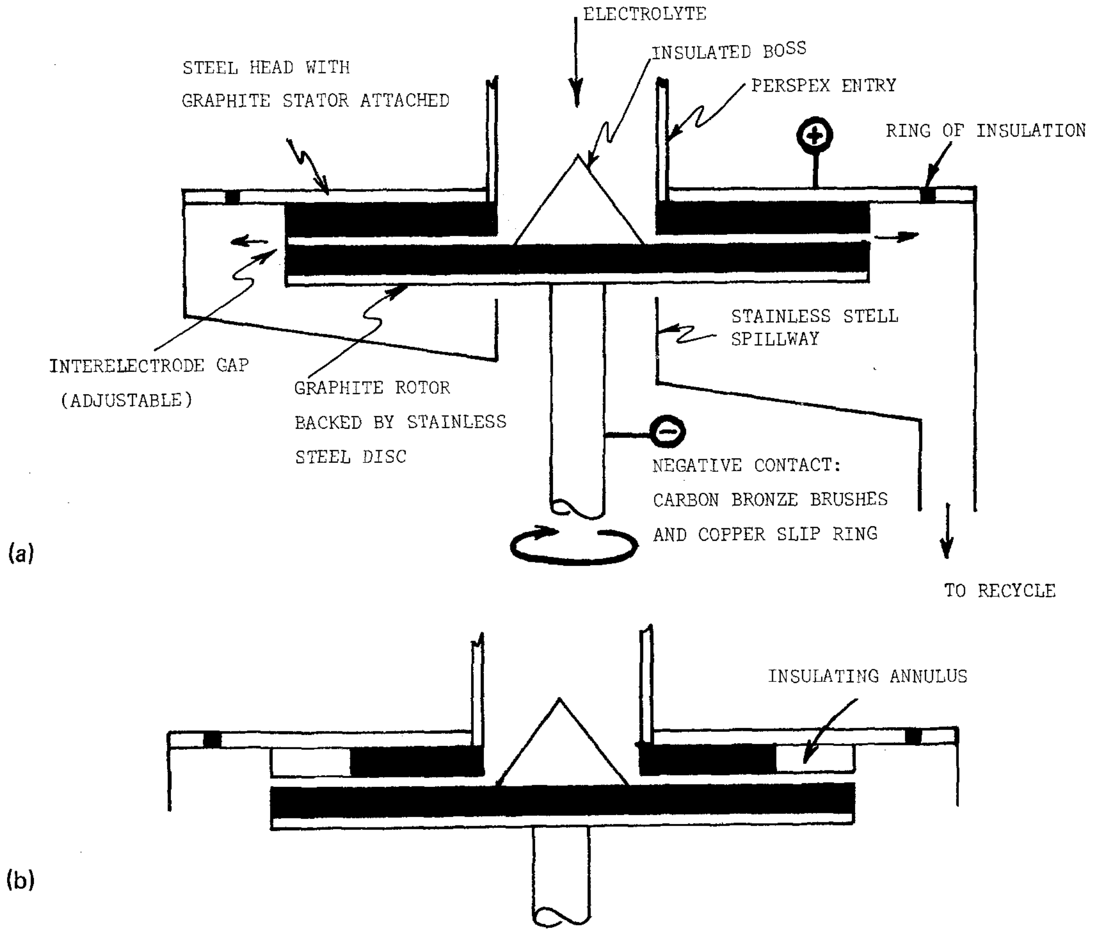


Fig. 1. Schematic diagram of cell (not to scale).

2. Reaction schemes

As the hypobromite/propylene oxide system has already received much attention [11, 12] it will only be outlined here. The initial step for both is the anodic oxidation of bromide

$$2\,Br^- \rightarrow Br_2 + 2e. \qquad (1)$$

The corresponding cathodic reaction is

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

so there is a natural tendency for the pH to increase during the reaction and further discussion will be limited to alkaline solutions. Hypobromite is formed in the bulk phase reaction

$$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+ \qquad (3)$$

$$HOBr \rightleftharpoons H^+ + OBr^-. \qquad (4)$$

There are a variety of possible loss reactions, but the most significant are the bulk phase disproportionation,

$$2HOBr + OBr^- \rightarrow O_3Br^- + 2Br^- + 2H^+ \qquad (5)$$

and further anodic oxidation of the hypobromite,

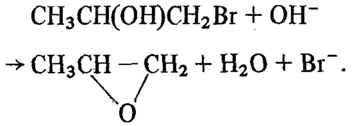
$$6OBr^- + 3H_2O \rightleftharpoons 2O_3Br^- + 4Br^- + 6H^+ + 3/2O_2 + 6e \qquad (6)$$

both reactions being significant at high concentration of hypobromite. Reaction 6 is particularly damaging to current efficiency. However the short residence time in the cell [2, 4] (typically 10 ms) and the extremely good mixing [7], which reduces high local concentrations of OBr^-, suggest that bromate formation due to Reactions 5 and 6 in a pump cell should be small. Of course, under good mixing conditions, the transfer of bromine to the cathode where it may be reduced provides another possible loss mechanism, so the overall performance of the cell for hypobromite production depends on the balance between electrochemical, chemical and transport rate processes.

The formation of propylene oxide is thought [12] to take place through the formation of propylene bromhydrin in a bulk phase reaction:

$$CH_3-CH=CH_2+HOBr\rightarrow CH_3CH(OH)CH_2Br. \qquad (7)$$

The bromhydrin is then thought to be hydrolysed in the locally very alkaline region close to the cathode [12]:



$$CH_3CH(OH)CH_2Br+OH^- \rightarrow CH_3CH-CH_2 \text{ (with O bridging CH and CH}_2) + H_2O+Br^-. \qquad (8)$$

Trial chemical experiments showed that the bromhydrin was readily formed, but was only slowly hydrolysed at the average pH in the recirculating electrolyte loop (about 9·5), whereas in the pump cell hydrolysis was virtually complete at exit.

Bromination of the propylene is also possible

$$CH_3-CH=CH_2+Br_2\rightarrow CH_3CHBr\,CH_2Br. \qquad (9)$$

The overall success of the process, therefore, depends on the relative rates of hydrolysis of Br_2 and the bromhydrin, as well as on the local conditions of mixing, dispersion and reaction during the transit time of the cell, as in the hypobromite case.

3. Experimental

The cell used in this work was an adaptation [2–4] of a Premier colloid mill, the carborundum stones of which had been replaced by disc electrodes 84 x 48 or 107 x 48 mm o.d./i.d. [Fig. 1(a)]. The anode was graphite and the cathode graphite or stainless steel. Polarization curves determined for 2% NaBr solution showed an inflexion at 900 mV (SCE), which was adopted as the working potential in the earlier experiments and maintained by a type 20/20A Chemical Electronics potentiostat. Above 900 mV oxygen was evolved but the potential could be increased to 1200 mV (SCE) without significant loss of current efficiency. The cell voltage was in the range 2·3–2·9 V.

Since, unavoidably, the rotor was in electrical contact with the structure of the mill through the bearings, the rotor was made cathodic and the electrically insulated stator anodic. All internal surfaces of the mill (largely stainless steel) were coated with epoxy film. Partly as a result of this work a new cell has been produced [13] in which only ceramic, polypropylene and the electrode material contact the electrolyte.

For most experiments the nominal gap setting was 0·15 mm and the flow rate was held at 4·5 l min^{-1} independently of rotational speed by use of a throttle valve. Under these conditions [2, 3] the pressure just inside the entry to the annular gap is sub-atmospheric [3], providing the ideal place for injection of propylene gas, which was subsequently highly dispersed by the rotational motion. Since propylene is only sparingly soluble in water, the presence of many small bubbles (with consequently large surface area) helps to re-establish saturation as dissolved propylene is consumed. Reaction at the phase boundary is also possible. Conversion of propylene was typically 40–70% during a single passage of the cell.

The electrolyte was 2% NaBr, 30 l of which was recirculated continuously and maintained at about 15° C to retain the propylene oxide in solution; the alternative of operating at a higher temperature to increase the current density and distil off the low boiling propylene oxide could not be adopted because the mechanical design of the original colloid mill did not allow the effective collection of exhaust gases, although this would be possible in the new design of cell [13].

The concentration of hypobromite was determined by titration with thiosulphate [14] and by u.v. adsorption [15] at 330 μm, the latter being the preferred method for continuous process control. Bromate was estimated by thiosulphate [14]. Propylene oxide was determined on a Pye 104 GLC using an internal standard.

4. Results

Fig. 2 shows the rate of production of hypobromite for various rotational speeds using an 84 x 48 mm graphite anode; clearly after the first few recycles the production rate at a given rotational speed is fairly constant. A local maximum

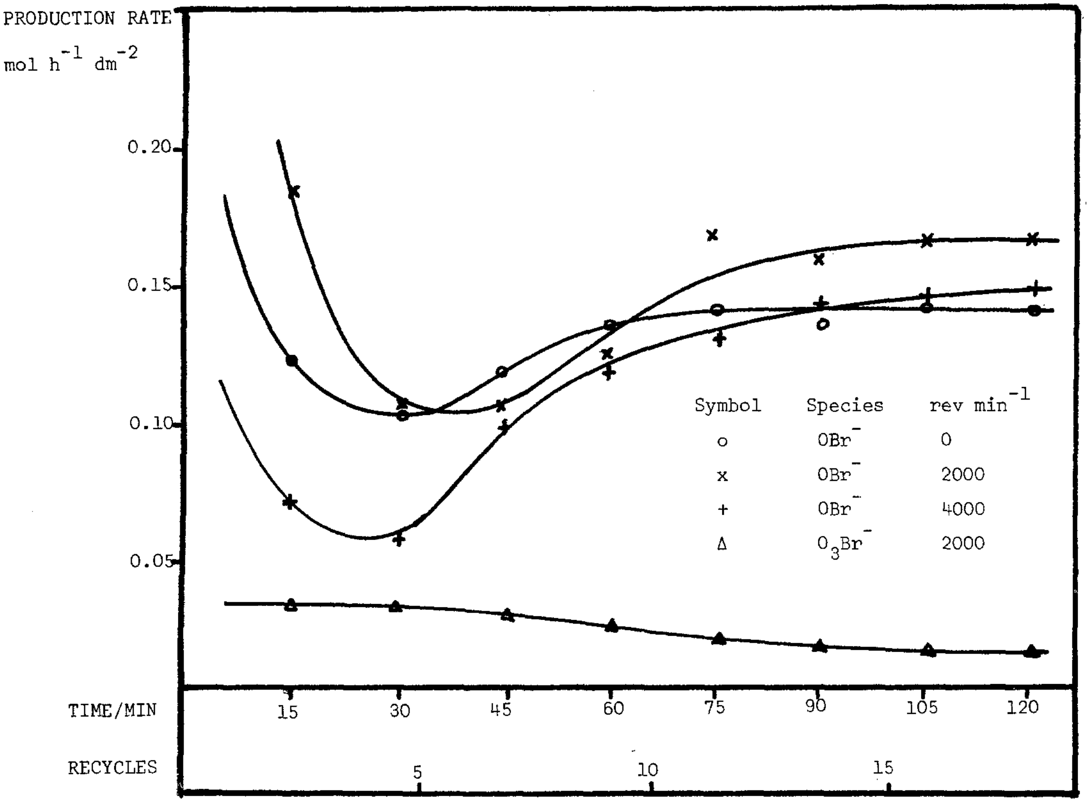


Fig. 2. Production rate of hypobromite/bromate as a function of conditions.

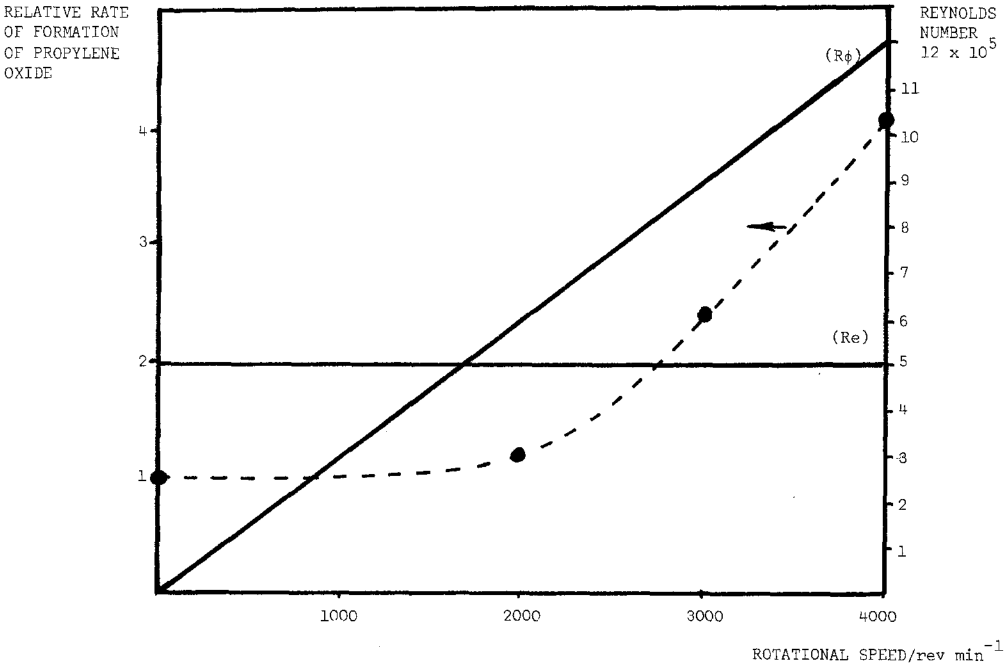


Fig. 3. Correlation of rate of formation of product and Reynolds number.

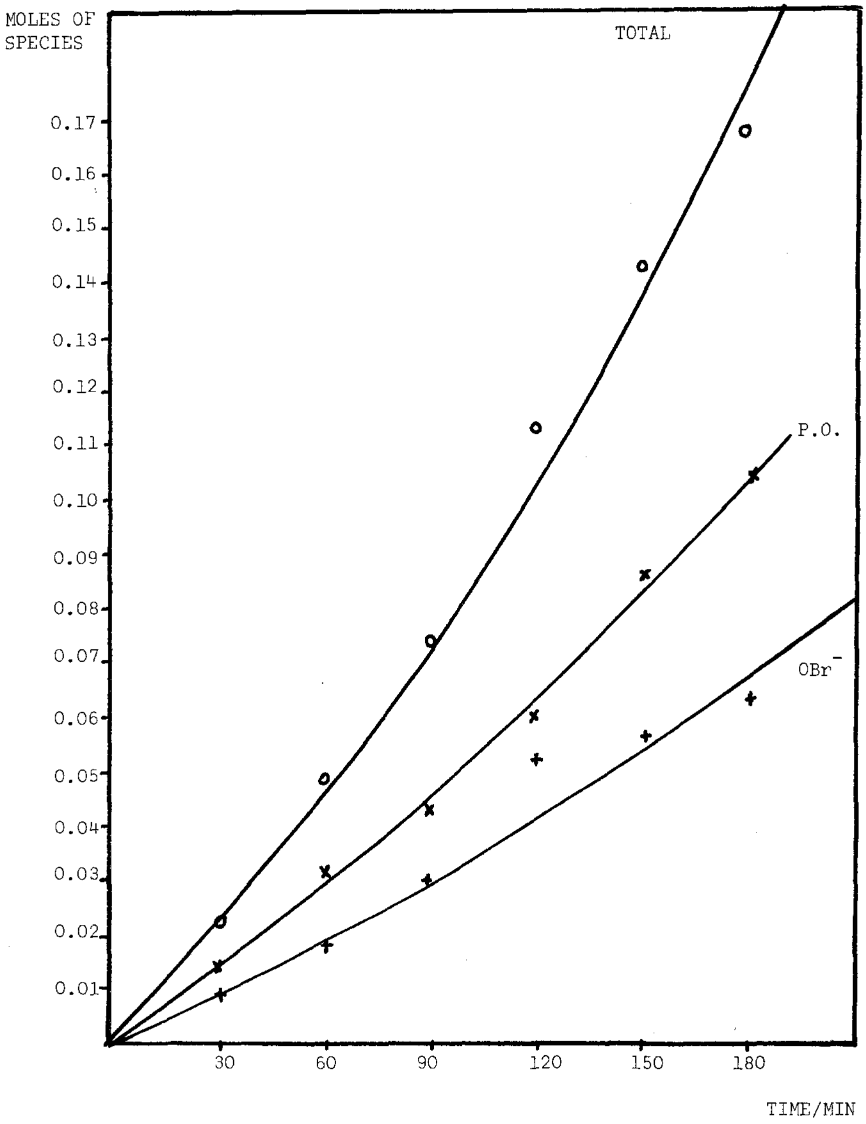


Fig. 4. Production of propylene oxide and hypobromite intermediate – one part stator.

exists at about 2000 rev min^{-1}, under which conditions the balance of formation and loss mechanisms outlined earlier is most favourable, but, as expected, the effect is not large. Under these conditions bromate is produced at about 10% of the rate of hypobromite. A summary of the relevant figures of merit is given in Table 1.

In the case of propylene oxide, mixing, and hence rotational speed, is much more important. Fig. 3 shows a superposition of the curve for the relative rate of formation of PO on top of the lines plotting Reynolds number versus rotational speed. Above 2000 rev min^{-1}, where (Re_ϕ) becomes greater than (Re), which was kept constant in these experiments, the rate of formation of PO increases with (Re_ϕ) i.e. mixing due to differential tangential motion. In these experiments the conversion of OBr$^-$ and propylene were both less than unity, so the extent of reaction was sensitive to changes in environment. Fig. 4 shows that the rate of formation of PO could not keep pace with the rate of formation of OBr$^-$; the current efficiency, based on PO, was of the order of 50%. However, by adopting a two part stator [Fig. 1(b)] in which the outer annulus was insulating (so that the electrochemical reaction was

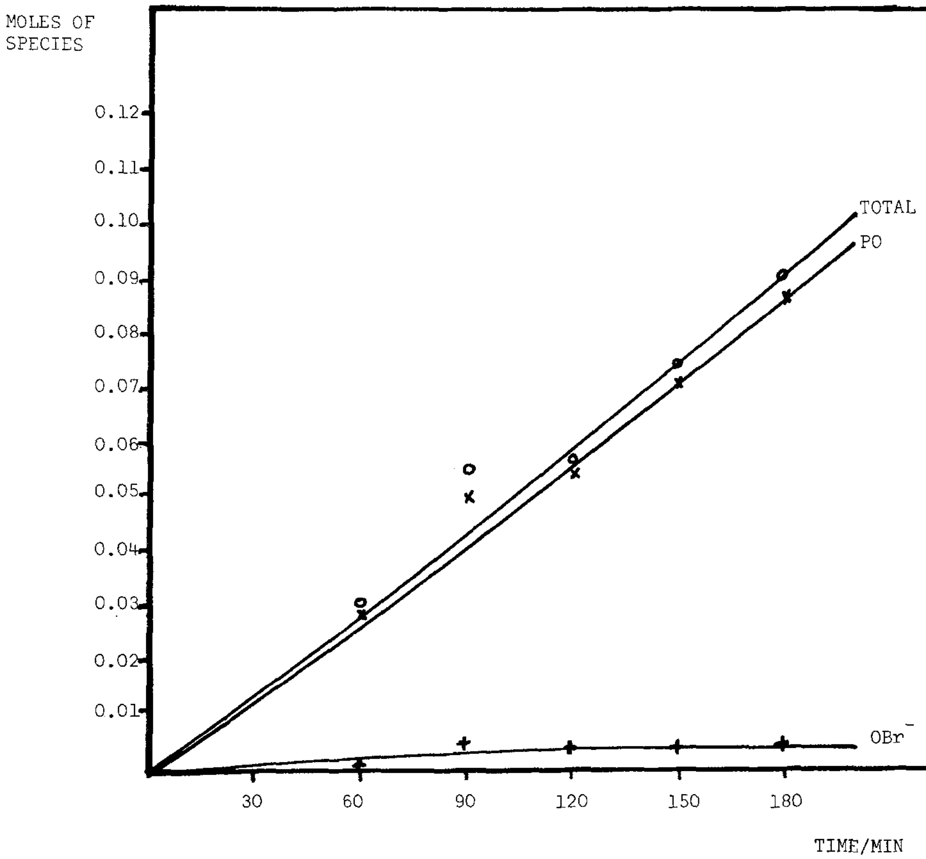


Fig. 5. Production of propylene oxide and hypobromite intermediate – two part stator (reduced electrode area).

suppressed but the electrochemically-generated conditions maintained) the residence time in the chemical zone was made twice as long as that in the electrochemical zone and the conversion of OBr^- went virtually to completion during the mean transit time of the cell (Fig. 5).

The dependence on cross gap mixing was further demonstrated by varying the gap while keeping other conditions approximately constant. Table 2 shows the maximum current efficiency at a nominal gap of 0·25 mm; at 0·15 mm the current efficiency is close to that found for the generation of HOBr alone (Table 1) showing that this, in fact, is not optimal, while at larger gaps presumably the intermediates are convected out of the cell before the reaction steps are complete. At a gap of 0·25 mm the conversion of OBr^- during passage through the cell was 100%, and of propylene about 57%, in a single pass; conversion of more than 70% of the propylene is possible even in these small cells, but at a lower current efficiency, i.e. not all the OBr^- is consumed.

Table 1. Production of sodium hypobromite from 2% NaBr, graphite anode, nominal gap 0·15 mm, 900 mV (*SCE*)

Rotational speed, n (10^3 rev min^{-1})	(Re_ϕ)	(Re)	*Current efficiency* (%)	*Production rate* (mol h^{-1} dm^{-2})	*Energy yield* (W h mol^{-1})	*Energy yield* (kW h kg^{-1})	*Production rate* (g h^{-1} dm^{-2})
0	0	5×10^5	77	0·136	206	1·73	16·2
2	$3{\cdot}7 \times 10^5$	5×10^5	84	0·168	189	1·59	20·0
3	$5{\cdot}5 \times 10^5$	5×10^5	77	0·147	170	1·43	17·5
4	$7{\cdot}4 \times 10^5$	5×10^5	76	0·151	205	1·72	18·0

Table 2. Production of propylene oxide, two-part stator, 3000 rev min^{-1}, *graphite anode,* 1200 mV (*SCE*)

Gap (mm)	(Re_{ϕ})	(Re)	*Current efficiency* (%)	*Production rate* (mol h^{-1} dm^{-2})	*Energy yield* (W h mol^{-1})	*Energy yield* (kW h kg^{-1})	*Production rate* (g h^{-1} dm^{-2})	*Mean residence time* (*total*) (ms)	*Conversion of propy-* (%)
0·15	$9{\cdot}0 \times 10^5$	$6{\cdot}7 \times 10^5$	79	0·089	196	3·38	5·16	10·9	44
0·25	$9{\cdot}0 \times 10^5$	$6{\cdot}7 \times 10^5$	100	0·114	156	2·69	6·61	10·9	57
0·635	$9{\cdot}0 \times 10^5$	$\sim 6 \times 10^5$	84	0·076	185	3·19	4·41	~ 11	38

In these experiments neither dibromopropane nor propylene glycol were detected.

5. Discussion

This work shows that in organosynthesis the space-time history of electrogenerated species can be equally as important as the electrochemical reaction which initiates the sequence. Significantly, in the production of the intermediate HOBr, the best conditions (Table 1) are where there is enhanced bulk mixing $[(Re_{\phi}) > 0]$ but the anode–cathode transport is not very efficient $[(Re_{\phi}) < (Re)]$. However the formation of PO, which relies on hydrolysis of the second intermediate in the alkaline catholyte layer, is enhanced in general by increasing (Re_{ϕ}), although at any given rotational speed there is an optimum gap size where the balance of production and loss reactions is most advantageous.

Although a full parametric survey was not carried out, Table 2 shows that in a pump cell it is possible to produce propylene oxide at a rate of at least 0·114 mol h^{-1} dm^{-2} for an energy cost of less than 2·7 kW h kg^{-1}. (The disparity of production rates in Tables 1 and 2 is due to the lower current density obtained in the experiments of 2, attributable to an inferior graphite electrode material.) More catalytic anode materials would increase the rate of production by a factor of two to five without significantly increasing the energy cost, while probably ten cells would be accommodated on a 10 cm length of shaft; the space time yield would then be about 5 mol h^{-1} dm^{-3}, 0·29 kg h^{-1} dm^{-3} or 7 kg day^{-1} dm^{-3}. Since the cells used in this work were small, high rotational speeds had to be used to ensure turbulent conditions, however mass transfer, mixing and dispersion depend on Reynolds number, not rotational speed *per se*; an optimal choice for an industrial process would no doubt be larger and would rotate more slowly [3].

In reactions in which mixing is important and surface and bulk phase kinetic rates are different, the electrochemical pump cell offers a means of substantially de-coupling mean residence time and mixing history by independent control of flow rate and rotational speed [7]. This feature is being exploited in other organosyntheses [16].

References

[1] M. Fleischmann, R. E. W. Jansson, G. A. Ashworth and P. J. Ayre, Brit. Prov. Pat. No. 18305, April 1974.

[2] G. A. Ashworth, Ph.D. Thesis, Southampton University (1977).

[3] R. E. W. Jansson and G. A. Ashworth, *Electrochim. Acta* (to be published).

[4] G. A. Ashworth, P. J. Ayre and R. E. W. Jansson, *Chem. Ind.* (1975) 385.

[5] G. A. Ashworth and R. E. W. Jansson, *J. Appl. Electrochem.* (1977) 309.

[6] I. H. Justinijanovic, Ph.D. Thesis, Southampton University (1974).

[7] J. Ghoroghchian and R. E. W. Jansson, unpublished work.

[8] F. Beck and H. Guthke, *Chim. – Ing. – Tech.* **41** (1969) 943.

[9] F. Kreith, *Int. J. Heat Mass Transfer* 9 (1966) 265.

[10] G. A. Ashworth and R. E. W. Jansson, *Electrochim. Acta* (to be published).

[11] T. Osuga and K. Sugina, *J. Electrochem. Soc.* **104** (1957) 448; N. Ibl and D. Landolt, *ibid* **115** (1968) 713; C. K. L. Tennakoon, Ph.D. Thesis, Southampton University (1972).

[12] F. Beck, Proc. I.U.P.A.C. Conference, Hamburg, September 1973.

[13] R. E. W. Jansson and R. J. Marshall, *Chem. Eng.* (315) November (1976).

[14] M. H. Hashmi and A. A. Ayan, *Analyt. Chem.* **35** (1963) 908.

[15] J. H. Howell and D. F. Boltz. *ibid* **36** (1964) 1799.

[16] R. E. W. Jansson and N. Tomov, *Chem. Eng.* (to be published).