

Development and evaluation of a Pt–Ru bimetallic catalyst based alkali concentrator in NaOH solutions

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An alkaline H₂–O₂ fuel cell based electrochemical alkali concentrator using Nafion[®]* 961 cation exchange membrane has been constructed. It is found that the concentrator can operate at a cell voltage around 0.6 V and the catholyte can be simultaneously concentrated to a level of 40 wt %, provided the outlet anolyte concentration is maintained at a level not below 23 wt %. Some possible directions for further improvement are indicated.

1. Introduction

In 1986, Taylor *et al.* indicated the possibility of concentrating 30 wt % alkali into commercially required 50 wt % alkali by an electrochemical alkali concentrator [1–3]. A broad description of the methods employed [4], evaluation of the economic aspects [5, 6] and analysis of data on a process development unit [7] have also been documented. However, this level of success has not yet been confirmed by any other workers and hence the present work. The fabrication of porous carbon electrodes [8, 9], and the evaluation of suitable cation exchange membranes for construction of an alkali concentrator have already been described [10]. In this paper, the construction and performance of an alkali concentrator is reported and discussed.

2. Experimental details

Pt–Ru bimetallic catalyst-based bilayer carbon electrodes were used as both hydrogen and oxygen electrodes. The gas diffusion layer consisted of acetylene black with a Teflon (polytetrafluoro ethylene) binder. The active layer facing the electrolyte solution also contained coconut-shell charcoal based activated carbon loaded with 2.5% Pt and 5.0% Ru by weight. Nickel mesh was used as the current collector and support for the electrode. The porous circular electrodes of 30 cm² geometric area were fabricated by hot pressing at 623 K for 2 min under a pressure of 150 kg cm⁻².

A diagram of the cylindrical alkali concentrator employed is presented in Fig. 1. The Nafion 961 membrane was fixed between the Pt–Ru catalyst based gas diffusion electrode disks using neoprene gaskets as spacers. The thickness of the gasket was usually 2 mm but was increased to 3 mm and 4 mm

for evaluating the *iR* drop due to increasing interelectrode distance. The electrolyte flows in the anolyte and catholyte chambers separated by the membrane were controlled by hydrostatic flow from a reservoir for slow flow rates and through a duostatic pump for higher flow rates. The hydrogen and oxygen gases were passed through the gas compartments on the other sides of the gas diffusion electrodes. The end plates and other spacers in the assembly were fabricated using Perspex. Two luggin capillaries connected these two electrodes to individual reference electrodes outside the cell assembly. This arrangement was used for individual electrode potential measurements.

3. Results and discussion

3.1. Discharge behaviour of alkali concentrators

For evaluating the discharge characteristic of the alkali concentrator under different experimental conditions, the initial concentrations of the electrolytes in both the anode and cathode compartments were kept at 30 wt %. The hydrogen and oxygen gas pressures were maintained at 50 mm over 760 mm Hg. Under these conditions, the open circuit potential of the alkali concentrator stabilized around 1.030 ± 0.020 V in about 30 min. The polarization measurements were initiated after achieving this stable open circuit potential.

The effect of electrolyte temperature on the discharge characteristics of the alkali concentrator is presented in Fig. 2. The lower and upper sets of curves correspond to the hydrogen and oxygen potentials, respectively. The actual potential difference between these two electrodes measured at different discharge rates (*E*_{cell}) are plotted in the middle of the Figure. The results clearly indicate a slight improvement in voltage response at higher temperature (Fig. 2). The overall cell voltages obtained experimentally at different current densities (*E*_{cell}) are slightly lower than those calculated

* Nafion[®] is a registered trademark of E.I. Du Pont de Nemours & Company.

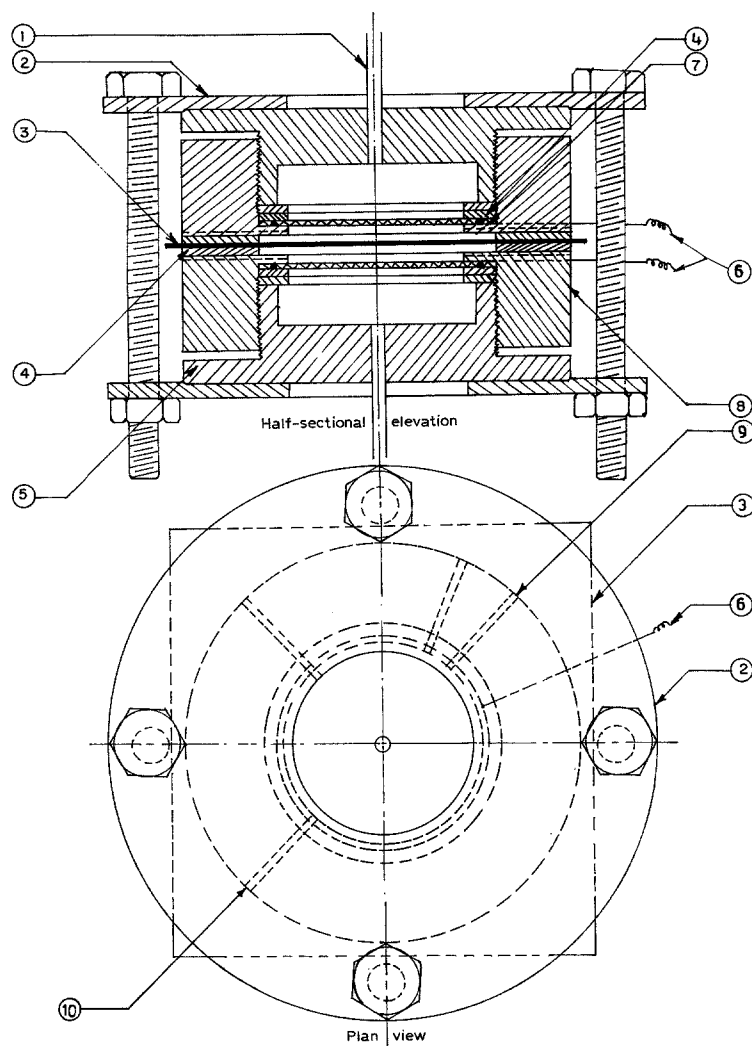


Fig. 1. The schematic representation of the alkali concentrator assembly. (1) Gas inlet, (2) cover plate, (3) membrane, (4) gasket, (5) gas chamber, (6) terminal wires, (7) electrode, (8) electrode holder, (9) electrolyte outlet, and (10) electrolyte inlet.

based on the algebraic sum of the anodic and cathodic potentials (E_{calc}). At an operating current density of 100 mA cm^{-2} , for example, this difference ($E_{\text{calc}} - E_{\text{cell}}$) is around 95 mV. This potential drop is due to the iR drop between the two electrodes, i.e. due to the electrolyte and membrane. In the earlier part of this work [9, 10] it was estimated that under identical experimental conditions, the iR drop due to the membrane is around 50 mV.

The effect of electrolyte resistance on the overall performance of the alkali concentrator is further confirmed by evaluating the influence of interelectrode distance on the discharge behaviour (Fig. 3). When the interelectrode distance was increased from 4 to 8 mm, both the anode and the cathode potentials remained fairly constant. But the actual cell voltage (middle curves) decreased drastically with increase in interelectrode distance. The cell voltage also decreased sharply with increasing current density (Fig. 3). The actual iR drop reached 150 mV at a current density of 100 mA cm^{-2} when the interelectrode distance was 8 mm. These results clearly indicate the need for minimizing the interelectrode dis-

tance to obtain maximum efficiency of the alkali concentrator.

The effect of anolyte and catholyte flow rates on the overall discharge characteristics of the alkali concentrator were evaluated by maintaining the flow rate of one of them at a constant level ($600 \text{ cm}^3 \text{ h}^{-1}$) and varying the other. It was found that neither the flow rate of anolyte nor that of catholyte have significant influence on the discharge behaviour of the alkali concentrator, as long as the concentration of the alkali solutions at the inlet point remains the same.

All experimental results presented above clearly indicate that the alkali concentrator can perform well at 348 K with an interelectrode distance of 4 mm at stagnant condition or at any optimum flow rate, under zero concentration gradient between anolyte and catholyte. Since the flow rate of the electrolyte in the individual compartments was sufficiently large ($600 \text{ cm}^3 \text{ h}^{-1}$) and the concentration of the electrolyte in both the compartments was high (30 wt% NaOH), the increase in alkali concentration in the catholyte due to oxygen reduction and the decrease in alkali concentration in the an-

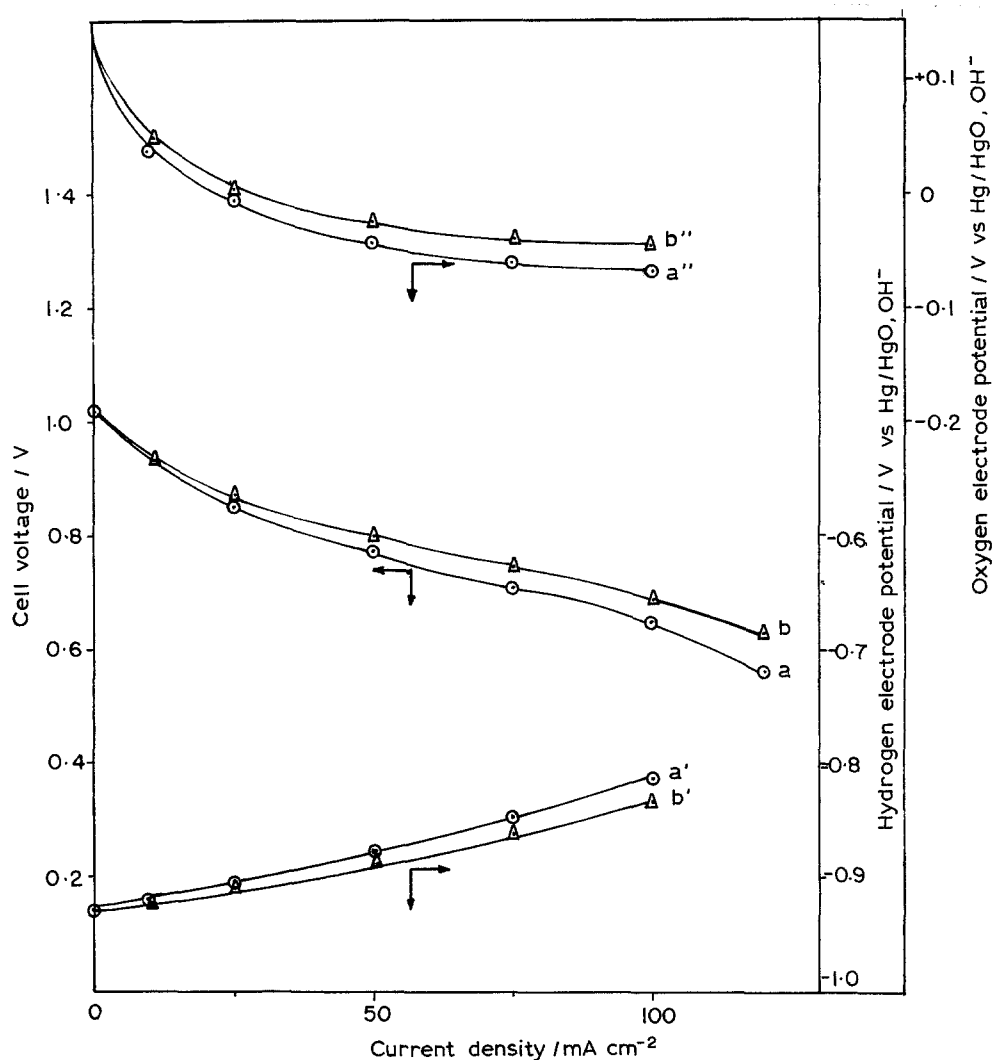


Fig. 2. Performance of the alkali concentrator at 333 K (a, a', a'') and at 348 K (b, b', b''). (Anolyte and catholyte: 30 wt % NaOH; flow rate of anolyte and catholyte: $120 \text{ cm}^3 \text{ h}^{-1}$; interelectrode distance: 4 mm).

lyte due to H_2 oxidation were quite small during the polarisation measurements. To evaluate the influence of concentration gradients on the discharge characteristics of the concentrator, a few discharge studies were carried out with different anolyte and catholyte concentrations. These results, presented in Table 1 and Fig. 4, indicate that when the difference in concentration between the two compartments is very high (20 wt % anolyte and 50 wt % catholyte) the cell voltage drops substantially. For example, at 100 mA cm^{-2} the vol-

tage drop can reach 240 mV and the attainable cell voltage from the electrochemical fuel cell reaction drops to 430 mV. Since the alkali solutions have maximum electrolytic conductivity at around 30 wt %, such a significant voltage drop is understandable.

3.2. Performance evaluation of alkali concentrator

Finally, the alkali concentrator was operated under different experimental conditions and the concen-

Table 1. Performance of the concentrator with different concentration of anolyte and catholyte (Temperature: 348 K; flow rate of anolyte and catholyte: $600 \text{ cm}^3 \text{ h}^{-1}$)

S	Anolyte concentration wt %	Catholyte concentration wt %	Concentration gradient wt %	At $i = 50 \text{ mA cm}^{-2}$					At $i = 100 \text{ mA cm}^{-2}$				
				E_{H_2} /V	E_{O_2} /V	E_{elect} /V	E_{cell} /V	iR /V	E_{H_2} /V	E_{O_2} /V	E_{elect} /V	E_{cell} /V	iR /V
1	30	30	0	-0.881	-0.024	0.857	0.801	0.056	-0.832	-0.045	0.787	0.685	0.102
2	25	35	10	-0.883	-0.035	0.848	0.785	0.063	-0.833	-0.060	0.773	0.660	0.113
3	25	40	15	-0.884	-0.048	0.836	0.764	0.072	-0.835	-0.085	0.750	0.610	0.140
4	20	40	20	-0.876	-0.058	0.818	0.722	0.096	-0.828	-0.113	0.715	0.541	0.174
5	20	50	30	-0.877	-0.081	0.796	0.670	0.126	-0.827	-0.155	0.672	0.430	0.242

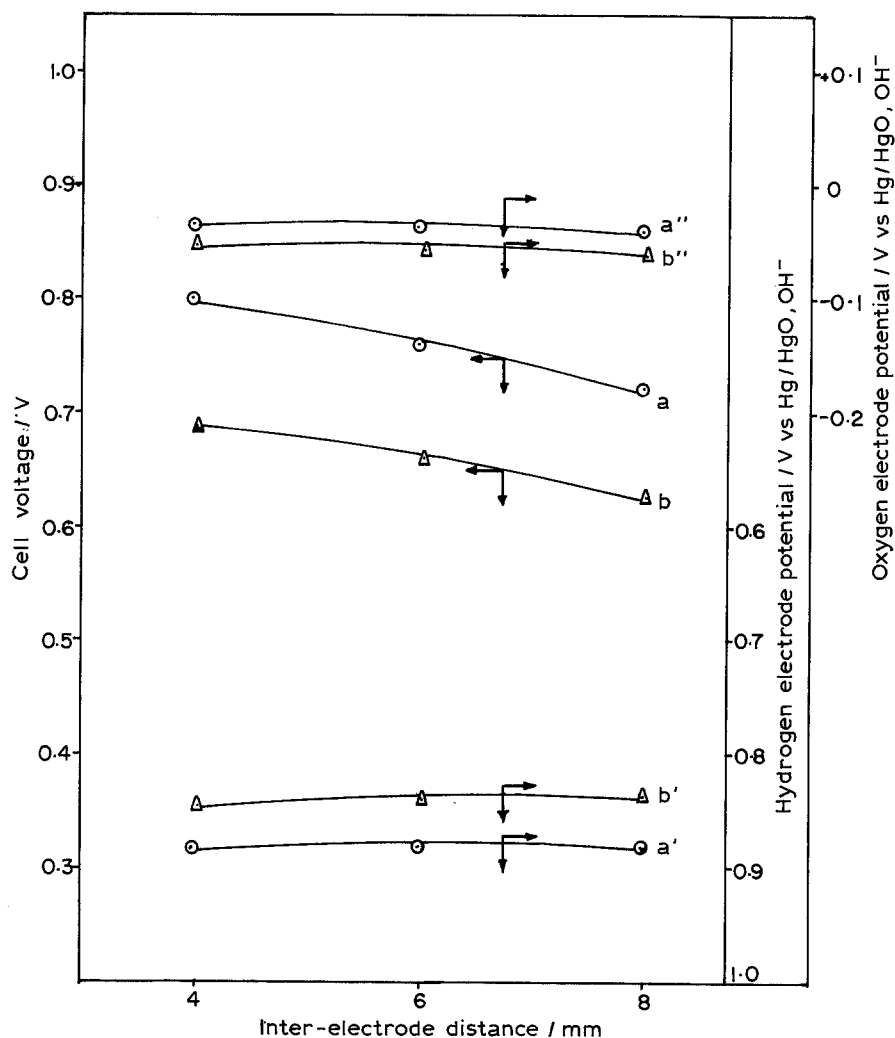


Fig. 3. Performance of the alkali concentrator with different interelectrode distance at 50 mA cm^{-2} (a, a', a'') and at 100 mA cm^{-2} (b, b', b'') current densities. (Anolyte and catholyte: 30 wt % NaOH; flow rate of anolyte and catholyte: $120 \text{ cm}^3 \text{ h}^{-1}$; temperature: 348 K).

tration buildup in the catholyte and its depletion in the anolyte were continuously monitored. Typical alkali concentration increases in the catholyte with time, at different anolyte alkali concentrations are presented in Fig. 5. It is seen that, at the optimum operating conditions, the catholyte concentration can increase up to 40 wt %. For this level of concentration buildup, it was found necessary to adjust and maintain the anolyte flow rate to keep its concentration at or above 23 wt %.

The influence of other parameters such as electrolyte flow rate, current density and anolyte concentration on the catholyte concentration – time behaviour were also investigated and the results are presented in Figs 6–8. These lead to the following conclusions:

- (i) Increase of catholyte flow rate leads to lower enhancement of outlet catholyte concentration but the concentrator efficiency improves considerably.
- (ii) Higher current density leads to better concentration enhancement and better concentrator efficiency.
- (iii) In general, as long as the alkali concentration gradient between the anolyte and catholyte compartment is low (less than about 15 wt %) and the

cell is operated at a sufficiently high current density, the alkali concentrator functions at the desired voltage around 0.6 V.

It should be noted that Taylor *et al.* [1–7] have claimed catholyte concentration build up to 50 wt %. However, from the published information [1–7] two differences between their work and the present work become obvious. Taylor *et al.* employed a rectangular reactor with path length up to 165 cm for achieving 50 wt % alkali concentration. The present cell employed circular electrodes which are only about 5 cm in diameter. A longer path length for the electrolyte in the reactor can possibly lead to higher concentration build up of catholyte. Secondly, along with alkali concentration, it is also important to achieve more power output with higher operating cell voltage. In the present work, the emphasis was always on achieving a cell voltage close to 600 mV. Taylor *et al.* have also indicated that the power output would decrease with higher concentration gradient between the catholyte and anolyte compartments [4], but the actual power output data under optimum conditions have not been reported by them.

Some possible approaches for future work may also

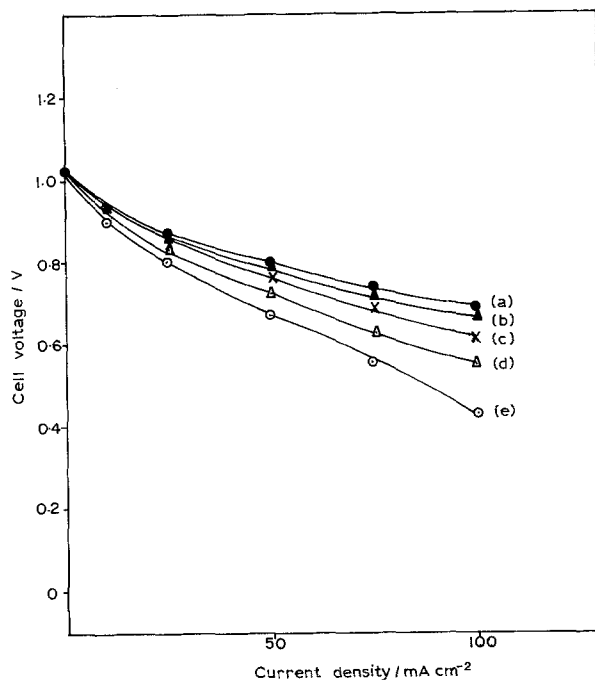


Fig. 4. Performance of the alkali concentrator with different concentrations of anolyte (A) and catholyte (C) at different current densities. (a) 30% A, 30% C, (b) 25% A, 35% C, (c) 25% A, 40% C, (d) 20% A, 40% C, and (e) 20% A, 50% C. (Temperature: 348 K; flow rate of anolyte and catholyte: $120 \text{ cm}^3 \text{ h}^{-1}$. Interelectrode distance: 4 mm).

be indicated here:

- (i) The effect of cell dimensions and cell design on alkali concentration without sacrificing the power output should be investigated.
- (ii) Another approach would be to employ dual stage

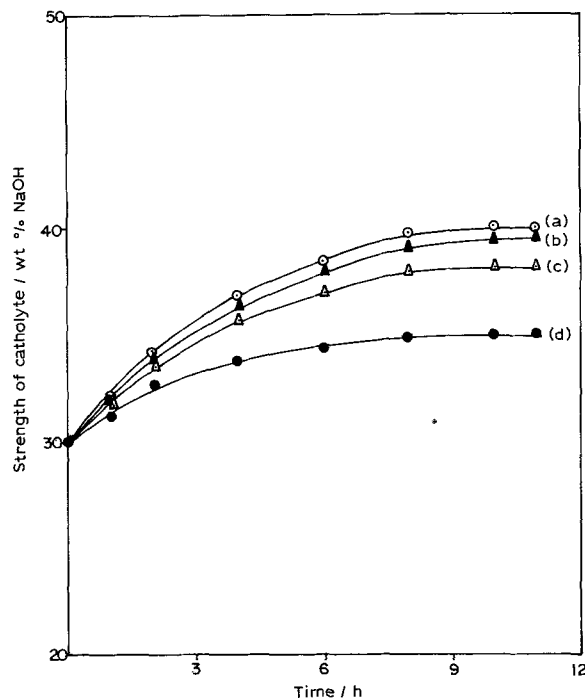


Figure 5. Performance of the alkali concentrator – effect of anolyte (outlet) concentration of (a) 25 wt %, (b) 23 wt %, (c) 21 wt %, and (d) 19 wt % on concentration buildup of catholyte. (Temperature: 348 K; flow rate of catholyte: $180 \text{ cm}^3 \text{ h}^{-1}$; interelectrode distance 4 mm; flow rate of anolyte: depending on the outlet concentration of anolyte).

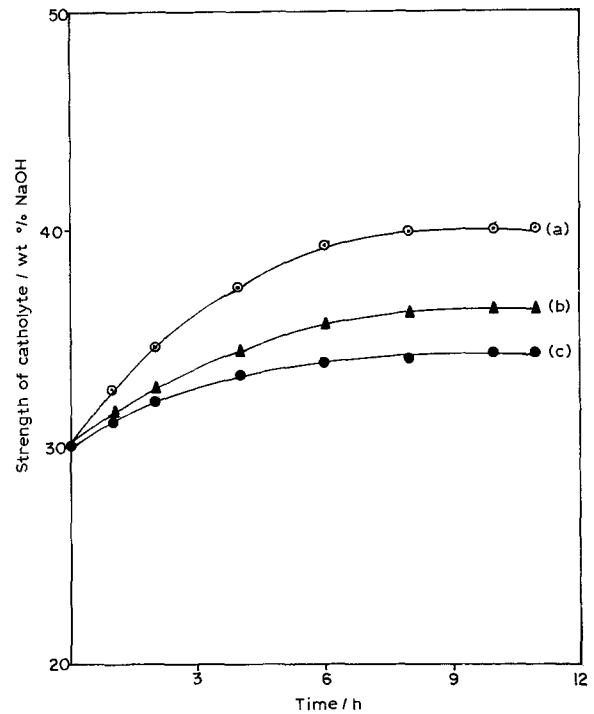


Figure 6. Performance of the alkali concentrator – effect of flow rate of catholyte for (a) $180 \text{ cm}^3 \text{ h}^{-1}$, (b) $360 \text{ cm}^3 \text{ h}^{-1}$, and (c) $540 \text{ cm}^3 \text{ h}^{-1}$ of catholyte. (Temperature: 348 K; interelectrode distance: 4 mm; anolyte-outlet concentration: 23 wt %).

buildup of concentration with 30 to 40 wt % alkali in the first stage and 40 to 50 wt % concentration in the second stage.

- (iii) Development of catalytic electrodes which can operate over longer periods at high current densities.
- (iv) Even Nafion 961 membrane used in the alkali concentrator presented here may undergo shrinkage at alkali concentrations beyond 40 wt % on continuous use. Chemical deactivation by the decarboxylations of COO^- groups is also possible. Development of bilayer membranes, which are more stable in stronger alkaline solutions, may enhance the potential applications of the alkali concentrator described here.

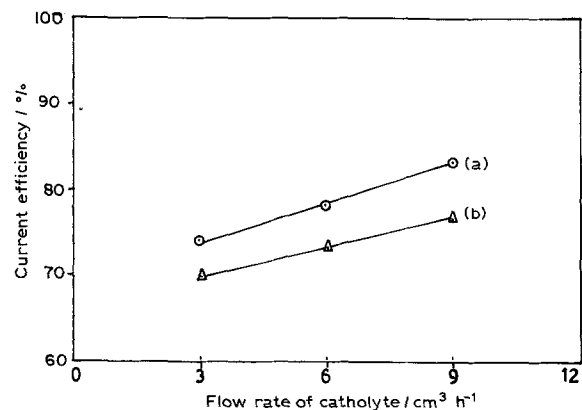


Figure 7. Performance of the alkali concentrator – effect of flow rate of catholyte on the current efficiency of the alkali concentrator: (a) 100, and (b) 50 mA cm^{-2} . (Temperature: 348 K, flow rate of catholyte: $180 \text{ cm}^3 \text{ h}^{-1}$; interelectrode distance: 4 mm; anolyte-outlet concentration: 23 wt %).

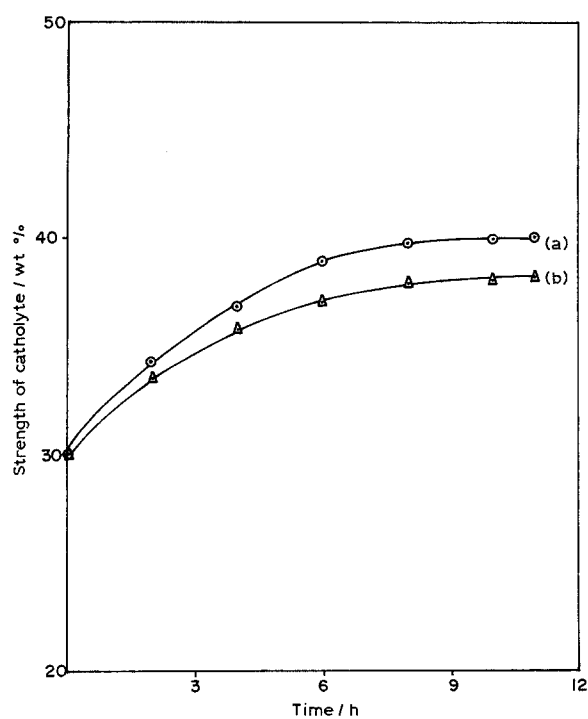


Fig. 8. Performance of the alkali concentrator – effect of current density on concentration buildup of catholyte: (a) 100, and (b) 50 mA cm⁻². (Temperature: 348 K; flow rate of catholyte: 180 cm³ h⁻¹; interelectrode distance: 4 mm; anolyte-outlet concentration: 23 wt %).

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