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The effect of corrugated membranes on salt splitting

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Abstract

An investigation of the electrohydrolysis of sodium sulfate using a corrugated Nafion® 117 membrane is reported. A comparison of the performance of a flat and corrugated Nafion® 117 in a two-compartment membrane electrolysis cell is made. Corrugating the membrane increased the active membrane area by 57% compared to the projected area. The effect of flow rate, current density and salt concentration on current efficiencies, transport properties and achievable product concentrations are presented. The results show a large improvement on transport properties, current efficiencies and product formation using corrugated membranes. Corrugated membranes gave an improvement of up to 77% on achievable base concentration and an increase of approximately 22% in current efficiency.

1. Introduction

The aim of this work was to investigate the performance of an ion-exchange membrane module using corrugated membranes. The use of corrugated membranes in ED cells can offer improved mass transport, increased membrane area, compared to the projected area of flat sheet membranes, and eliminate the cell spacers used in traditional designs. It is expected that enhanced mass transfer rates, achieved by using a corrugated flow arrangement, will result in improved chemical recovery efficiency and energy efficiency. Corrugated membranes and dimpled membranes have previously been suggested as a means of improving mass transport or increasing membrane filtration area [1–6]. The configurations and membrane materials used were different to that applied in this work.

Corrugated membranes can reduce concentration polarization at the membrane surface and potentially reduce membrane fouling and improve energy consumption. Scott et al. [7] showed that membrane filtration with corrugated membranes enhanced the flux by approximately 160% in comparison to a flat membrane. This enhancement was achieved through a combination of turbulence promotion near the membrane and increase in membrane area on a module volume basis. The reduction of concentration polarization in microfiltration using helical corrugated tubular membranes was clearly demonstrated by Broussous et al. [8]. In pervaporation, the flux across selective membranes can potentially be increased by at least five times by using corrugated membranes [9].

The process of salt splitting, a focus of this work, is an attractive area for electrochemical technology. The splitting of the salts to their original constituents is highly desirable to minimize chemical consumption, effluent treatment costs and to enable reuse of acids and bases. The electrohydrolysis of Na_2SO_4 has been known for some time. Stender and Seerak in 1935 [10] described a process for the recovery of sulfuric acid from sodium sulfate using a three-compartment diaphragm cell. The Electrosynthesis Company, in a joint project with the Ormiston Mining Company have, more recently, described a modified three-compartment cell process which converts sodium sulfate into ammonium sulfate and sodium hydroxide [11].

Ceramic membranes have been used in the electrohydrolysis of an aqueous solution of sodium salt to produce acid and base [12, 13]. Combinations of cation- and anion-exchange membranes in conjunction with the electrochemical dissociation of water to protons and hydroxide ions have been widely used to hydrolyse sodium salts [14]. Bipolar membranes have also been tested for sodium sulfate splitting [15] with current efficiencies reported at 78% for both the acid and base [16]. Rakib [17] determined the sodium transport number and the water flow through a Nafion® 350 membrane for sodium sulfate electrochemical splitting.

The major aim of this work was to demonstrate the potential for improved electrohydrolysis of sodium sulfate using corrugated membranes compared with that achieved with flat membranes.

The experimental tests measured the change in ion concentrations as a function of time; these data were then used to calculate key performance measures of current efficiency and transport number.

Current efficiency (Φ) is a crucial parameter in electromembrane applications and is closely related to membrane behaviour. It represents the proportion of charge used in producing a desired product over the charge passed through the system. It relates the performance of a process to a theoretical maximum and can be determined from:

$$\Phi = \frac{nFV\Delta C}{I\Delta t} \tag{1}$$

where n is the number of electrons transferred, F the faradaic constant (96 484.5 C mol^{-1}), V the volume of the electrolyte solution (dm^3), ΔC the change in concentration (mol dm^{-3}), I the current (A) and Δt the time interval (s).

The sodium ion flux or permeation rate, N_{Na^+} (equiv. m^{-2} s^{-1}), is determined as the molar rate of species passing through unit area of membrane, per unit time.

$$N_{\text{Na}^+} = \frac{(n_{\text{Na}^+})_{t+\Delta t} - (n_{\text{Na}^+})_t}{A\Delta t} \tag{2}$$

where, n_{Na^+} is the number of moles of sodium, Δt the time difference (s) and A the membrane area (m^2).

Considering this, the sodium transport number, defined as the ratio of sodium ion flux through the membrane per total charge passed through the cell, is given by

$$t_{\text{Na}^+} = F\frac{(n_{\text{Na}^+})_{t+\Delta t} - (n_{\text{Na}^+})_t}{I\Delta t} \tag{3}$$

The transport number and current efficiency are equivalent measures of performance of the cell, that is,

$$t_{\text{Na}^+} = \frac{\Phi[(n_{\text{Na}^+})_{t+\Delta t} - (n_{\text{Na}^+})_t]}{nV\Delta C} \tag{4}$$

2. Experimental details

2.1. *Experimental apparatus*

In all the experiments a two-compartment electrohydrolysis flow cell was used. The cell consisted of a platinum oxide based coated titanium anode (Cumberland Engineering, proprietary anode) and a stainless steel cathode each 100 cm^2 in area. To minimise the cell voltage, and hence the power consumption, the inter-electrode gap was 3 mm. The installed membrane area was 140 cm^2 for the flat membrane and 220 cm^2 for the corrugated membrane giving an increase of 57% on the actual membrane area. Figure 1 shows design characteristics of the two-compartment cell used. The anolyte solution contained the desired concentration of sodium sulfate while the catholyte contained dilute NaOH solution (0.2 M). The circulation of the solutions from two 1 dm^3 glass reservoirs to the cell was by peristaltic pumps. Both anolyte and catholyte compartments were

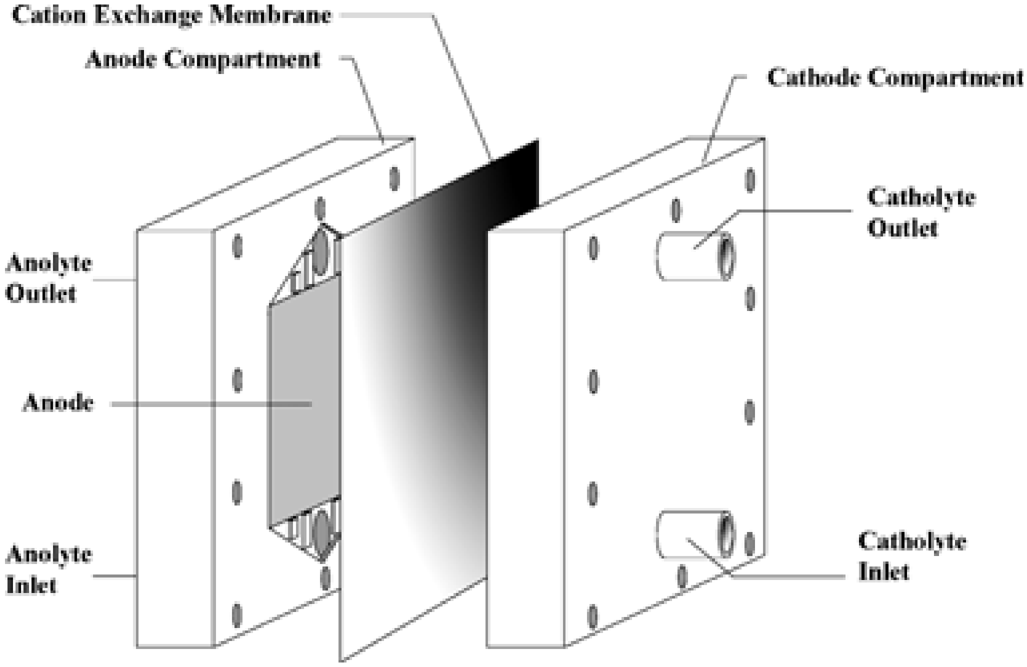

Fig. 1. Design characteristics of the two-compartment cell.

circulated at the same flow rate. When corrugated membranes were used the flow was perpendicular to the directions of the corrugations.

Throughout the electrohydrolysis, the solutions in the reservoirs were stirred with magnetic stirrers. Each experiment proceeded under batch recirculation conditions for two hours at the chosen current density, flow rate and initial salt concentration. Direct current was provided by a Farnell d.c. power supply (max. 70 V/30 A). All experimental current densities are based on the actual surface area of the membranes.

Samples from the catholyte and the anolyte were taken every 15 min. The concentrations of acid and base were measured volumetrically by titration with NaOH and H_2SO_4, respectively. Phenol red was used as an indicator. During each run the cell voltages were also recorded.

2.2. *Corrugated membranes*

The membranes to be corrugated were pretreated by boiling successively, in distilled water, 3% hydrogen peroxide at 80 °C, sulfuric acid (0.5 M) and again distilled water. Corrugated membranes were prepared by mechanical pressing of flat sheet membranes between metal dies at 100 °C and 6 tons pressure. Corrugation did not result in mechanical damage of the membrane. Pressing of the flat membrane creates small channels on its surface (corrugations). Each channel in the membrane is 2 mm wide and 1 mm high. The typical corrugated membrane structure is shown in Figure 2. When used in the cell, the gap between the electrode and the peak of the corrugated membrane was 1 mm. Consequently corrugations provide a larger surface area through which the ions can pass.

A Nafion® 117 membrane was used in all tests. From the H^+ form it was transferred to Na^+ form by pretreatment with NaCl. After pre-treatment, the membrane was stored in room- temperature deionized water. At the end of each experiment the membrane was washed twice with deionized water prior to reuse. The performance of each membrane was studied, under the following conditions:

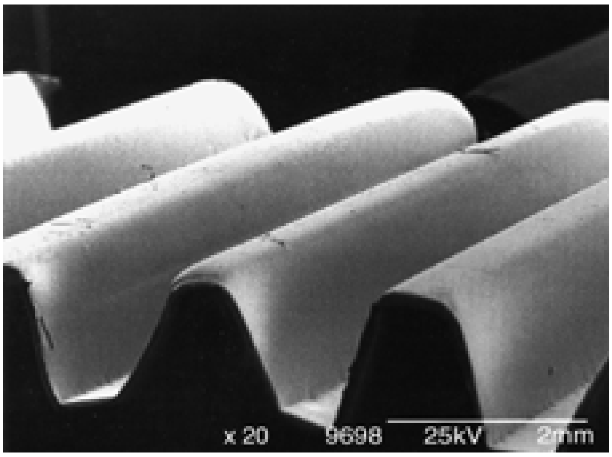

Fig. 2. SEM of corrugated Nafion® membrane.

(i) Flow rate (0.27, 0.45, 0.62 and 0.84 $dm^3\ min^{-1}$). Flow rates were equivalent to Reynolds numbers in the range of 81 to 252 based on the open channel hydraulic mean diameters of 1.96 and 2.91 mm for flat and corrugated membranes, respectively, using the physical properties of sodium sulfate solution. A 2.0 M Na_2SO_4 solution and a flow rate of 0.84 $dm^3\ min^{-1}$ was considered for calculating Reynolds numbers.

(ii) Current density (500, 1000, 1500 and 2000 A m^{-2}).

(iii) Salt concentration (0.5, 1.0 and 2.0 mol/dm^{-3} (M)).

All runs were performed at room temperature (20 °C). When experiments were used to determine the influence of one parameter the other variables were kept constant at the standard conditions of 0.84 $dm^3\ min^{-1}$, 1000 A m^{-2} and 2.0 M Na_2SO_4.

3. Results and discussion

The process of electrohydrolysis (EHD) results from the combined action of the electrolyses of water and ion transfer through selective membranes.

$$\text{At the anode:}\quad H_2O \rightarrow 2\,H^+ + \frac{1}{2}\,O_2 + 2\,e^-$$

$$\text{In the anolyte:}\quad 2\,H^+ + SO_4^{2-} = H_2SO_4$$

$$\text{At the cathode:}\quad H_2O + 2\,e^- \rightarrow OH^- + \frac{1}{2}\,H_2$$

$$\text{Membrane transport:}\quad Na^+|\text{anode} \rightarrow Na^+|\text{cathode}$$

$$\text{In the catholyte:}\quad Na^+ + OH^- = NaOH$$

In addition there will be transport of protons across the membrane which causes inefficiency

$$H^+|\text{anode} \rightarrow H^+|\text{cathode}$$

The operating conditions, experimental current efficiencies and sodium ion fluxes for the flat and the corrugated Nafion® 117 membranes are summarized in Table 1. Current densities and the other experimental parameters were the same for both membranes. However, current density was based on the actual area of the membrane. Consequently the current was higher for the cell where the corrugated membrane was installed due to the higher exposed area of this membrane. The results clearly indicate an improvement in current efficiency and ionic flux for the corrugated membrane compared to the flat sheet membrane.

3.1. *Influence of operating parameters*

The effect of flow rate on the current efficiency for the flat and corrugated Nafion® 117 membrane is given in

Table 1. Experimental conditions, current efficiencies, sodium ion fluxes and regenerated sodium hydroxide concentrations for the flat and the corrugated Nafion® 117 cation-exchange membranes

Run	Flow rate /dm min^{-1}	C.D. /A m^{-2}	Na_2SO_4 /M	Cell voltage /V		Current efficiency /%		Na$^+$ fluxes /equiv m^{-2} s^{-1}		NaOH concentration	
				flat Naf.®	corr Naf.®	flat Nafion® 117	corr. Nafion® 117	flat Nafion® 117	corr. Nafion® 117	flat Nafion® 117	corr. Nafion® 117
1	0.27	1000	2	4.66	4.74	78.9	96.8	0.0082	0.0103	0.84	1.48
2	0.45	1000	2	4.52	4.50	72.1	97.3	0.0074	0.0105	0.73	1.52
3	0.63	1000	2	4.68	4.37	80.7	96.2	0.0084	0.0102	0.83	1.48
4	0.84	1000	2	4.37	4.39	80.1	92.0	0.0081	0.0095	0.89	1.46
5	0.84	1000	1	4.48	4.45	75.9	88.3	0.0079	0.0092	0.73	1.19
6	0.84	1000	0.5	4.59	4.00	52.5	68.8	0.0054	0.0071	0.45	0.76
7	0.84	500	2	4.35	3.77	71.9	98.4	0.0039	0.0052	0.46	0.80
8	0.84	1500	2	4.61	4.59	79.9	93.3	0.0117	0.0150	1.21	1.96
9	0.84	2000	2	5.14	4.85	79.7	86.6	0.0165	0.0182	1.45	2.10

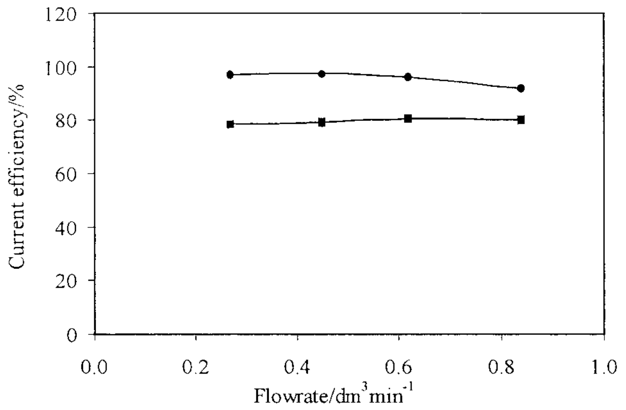

Fig. 3. Comparison of current efficiencies for flat and corrugated Nafion® 117 at four different flow rates (0.27, 0.45, 0.63 and 0.84 dm^3 min^{-1}) at 2.0 M initial salt concentration and the current density of 1000 A m^{-2}. Key: (●) corr. Nafion® 117; (▲) flat Nafion® 117.

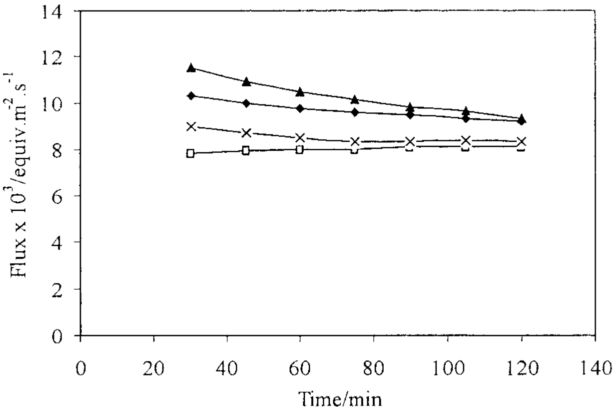

Fig. 4. Comparison of flux rates for flat and corrugated Nafion® 117 at the current density of 1000 A m^{-2} with initial salt concentration of 2.0 M at two flow rates. Key: (▲) corrugated Nafion® 117, 0.45 dm^3 min^{-1}; (x) flat Nafion® 117, 0.45 dm^3 min^{-1}; (♦) corrugated Nafion® 117, 0.84 dm^3 min^{-1}; (□) flat Nafion® 117, 0.84 dm^3 min^{-1}.

Figure 3. It can be seen that flow rate, over the range considered, did not significantly affect the current efficiency; the dominant mass transport factor is the presence or not of corrugations. The corrugated membrane enhanced the current efficiency by approximately 15% compared with the flat membrane. The improvement in current efficiency for the corrugated Nafion® 117 was associated with an increase in mass transport and the higher current which resulted in a higher sodium ion flux. The cation exchange membrane was possibly in the alkaline state, which means that it permitted the transfer of hydroxide ions from the catholyte to the anolyte. The current efficiency was enhanced in the case of the corrugated membrane because the difference in the sodium ion flux and the flux of hydroxide ions was increased.

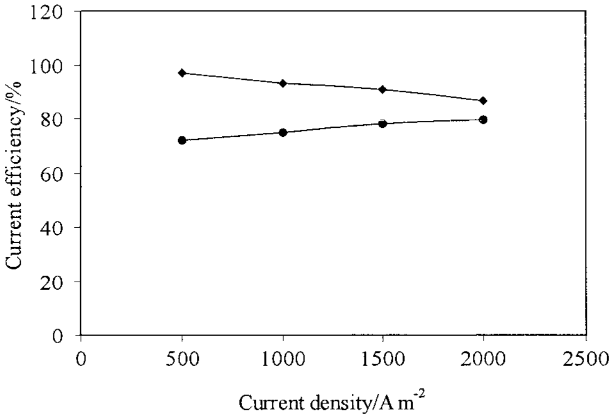

Fig. 5. Comparison of flat and corrugated Nafion® 117 cation-exchange membranes in terms of current efficiency at four different current densities (500, 1000, 1500 and 2000 A m^{-2}), at the flow rate of 0.84 dm^3 min^{-1} and 2.0 M initial salt concentration. Key: (♦) corrugated Nafion®; (●) flat Nafion®.

Figure 4 shows a comparison of the variation in sodium ion flux rate with time for the two membranes at two flow rates. An improvement of approximately 16% in sodium ion flux was achieved using the corrugated membrane. In particular at low flow rates the increases in current efficiency and sodium ion flux on corrugating the membrane were significant (Table 1). Figure 5 shows the influence of current density on the sodium ion current efficiency. The improvement in current efficiency with corrugated membranes was more noticeable at the lower current densities. Increases of 27%, 12%, 13% and 7% in the current efficiency were achieved using corrugated membrane at current densities of 500, 1000, 1500 and 2000 A m^{-2}, respectively.

Water transport across each membrane is due to electroosmosis. Due to the hydrophobic nature of the perfluorosulfonic membrane, water transport concerns mainly water of the ion hydration sphere. The amount of water transferred, mainly with the sodium ion, is proportional to the sodium transport number. Each mole of sodium transfers between 4 and 5 moles of water. Hydrogen ions take about three (or less) moles water per mole of ion [13]. Since the transport number, and hence the sodium flux, were higher with the corrugated membrane a greater difference in the volumes of the anolyte and the catholyte was observed during electrolyses with the latter membranes.

The variation in concentration of sodium hydroxide with time, at three current densities and a flow rate of 0.84 dm^3 min^{-1} and initial salt concentration (2 M), is shown in Figure 6. Productivity was greater at a higher current density, but because the cell voltage was higher at higher current density, as shown typically in Figure 7, the energy efficiency per unit product decreased. However, a steady decrease in the cell voltage with time was observed in all the experiments due to the increased conductivity of the regenerated sulfuric acid. The steady increase in the conductivity and the steady decrease in the pH of the feed compartment were due to replacement of sodium ions by hydrogen ions. Sodium ions have an equivalent ionic conductivity of approximately 50 cm^2 Ω^{-1} $equiv^{-1}$ compared to a value of approximately 350 cm^2 Ω^{-1} $equiv^{-1}$ for hydrogen ions [16]. Simultaneously the sodium flux rates through each membrane were enhanced at higher current densities although a slight decrease in the current efficiency was observed at higher current densities.

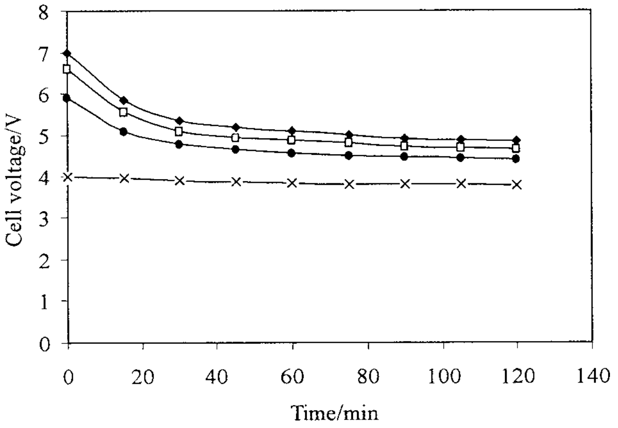

Fig. 7. Variation of cell voltage as a lapse of time with the corrugated Nafion® 117 at four different current densities. Key: (♦) 2000, (□) 1500, (●) 1000 and (×) 500 A m^{-2}. Flow rate 0.84 dm^3 min^{-1} and salt concentration 2.0 M in all runs.

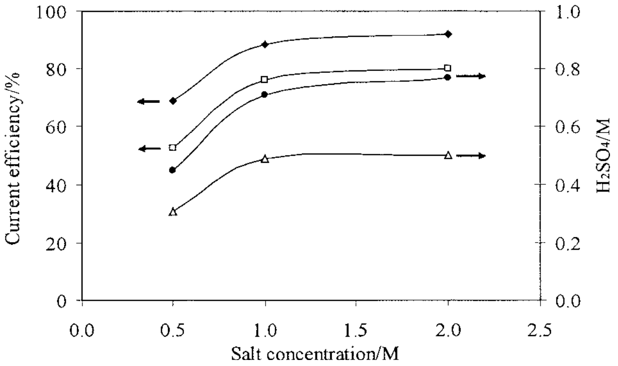

Fig. 8. Current efficiencies and regenerated sulfuric acid concentrations against available salt concentration for the flat and corrugated Nation® 117 membranes at two initial sodium sulfate concentrations; 0.5 and 2 M. Flow rate 0.84 dm^3 min^{-1} and current density 1000 A m^{-2} in all runs. Key: (♦) corrugated Nafion®, 2.0 M Na_2SO_4; (□) flat Nafion®, 2.0 M Na_2SO_4; (●) corrugated Nafion®, 0.5 M Na_2SO_4; (△) flat Nafion®, 0.5 M Na_2SO_4.

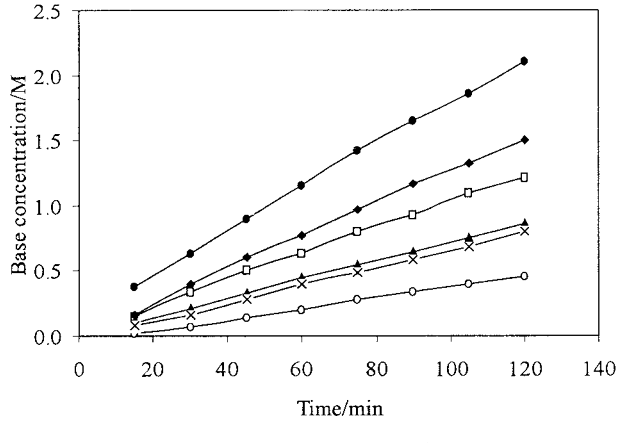

Fig. 6. Comparison of flat-corrugated Nafion® 117 cation-exchange membranes in terms of achievable base concentrations at the flow rate of 0.84 dm^3 min^{-1}, and 2.0 M initial salt concentration at three different current densities. Key: (●) corrugated Nafion®, 1500 A m^{-2}; (□) flat Nafion®, 1500 A m^{-2}; (♦) corrugated Nafion®, 1000 A m^{-2}; (×) flat Nafion®, 1000 A m^{-2}; (▲) corrugated Nafion®, 500 A m^{-2}; (○) flat Nafion®, 500 A m^{-2}.

Figure 8 shows the influence of initial sodium sulfate concentration on current efficiencies and achievable sulfuric acid concentrations for the flat and the corrugated Nafion® 117 membrane. The data clearly illustrate the benefit, in terms of higher transport number, of using corrugated membranes. Figure 9 shows the variation in NaOH concentration with time at three ionic strengths, using both types of membrane. The superiority of the corrugated membranes over the flat membrane is demonstrated. Even at a relatively low concentration of 0.5 M, the regenerated base concentration achieved with the corrugated membrane was higher than that with the flat membrane with a 2 M concentration. It is clear that operation at higher salt concentrations is preferred. The faradaic process at the anode resulted in the generation of protons in the feed compartment and led to a reduction in current efficiency for sodium transport, due to competing transport of hydrogen ions across the cation-exchange membrane. As the duration

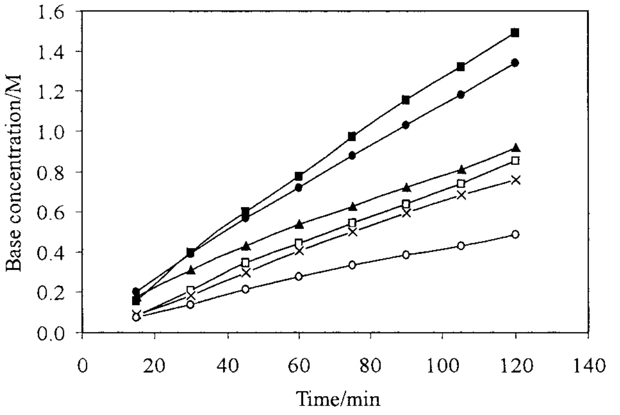

Fig. 9. Comparison of flat and corrugated Nafion® 117 cation-exchange membranes in terms of achievable base at the flow rate of 0.84 dm^3 min^{-1} and current density of 1000 A m^{-2} at three different initial salt concentrations. Key: (◆) corrugated Nafion®, 2.0 M Na_2SO_4; (●) corrugated Nafion®, 1.0 M Na_2SO_4; (▲) corrugated Nafion®, 0.5 M Na_2SO_4; (□) flat Nafion®, 2.0 M; (×) flat Nafion®, 1.0 M; (○) flat Nafion®, 0.5 M Na_2SO_4.

of salt splitting increased the current efficiency also decreased, due to salt depletion.

It is noteworthy that the corrugations did not appear to affect the selectivity of the membrane. The selectivities of the flat and corrugated Nafion® 117 membranes calculated using the equation derived in [18] were quite high. The sulfate transport number was 7×10^{-4} for the flat Nafion® 117 and 5×10^{-4} for the corrugated. This factor is crucial in cases where high selectivity of the CEM is required in order to limit salt migration. No loss of selectivity for the two kinds of membrane was observed.

Also, there is an increase in regenerated base concentration in the case of corrugated membranes (Table 1). An increase of about 74% in acid concentration was also achieved under the whole range of flow rates considered. The enhancement in flux due to corrugations, (i.e., the ratio of the total sodium flux across a corrugated membrane to the total flux across the similar flat membrane) ranged between 1.1 and 1.4 for all the runs.

Figure 10 compares the current efficiency for sodium hydroxide production, for the flat and corrugated membranes, as a function of charge passed under otherwise similar operational conditions. The corrugated membrane gave some 14–16% improvement in efficiency and the improvement was more prominent in the initial stages of the experiment (up to 1300 °C).

3.2. *Cell voltage characteristics*

Table 1 gives typical cell voltages for EHD with both flat and corrugated membranes. Up to 2000 A m^{-2}, the maximum current density employed in this work, there was a steady rise in voltage with current. Cell voltages with the corrugated membrane were similar, if not lower, to those using the flat membrane, despite the much higher current densities in the former case. This suggests improved energy consumption per kg of sodium hydroxide produced with the corrugated membrane. However, it should be born in mind that the voltage given is the final voltage achieved and, in the case of the corrugated membrane, reflects the higher acid and base concentrations produced. The energy consumption for this work with the corrugated membranes is in the range 2.64 to 5.84 kWh kg^{-1} for the current density range 500 to 2000 A m^{-2}.

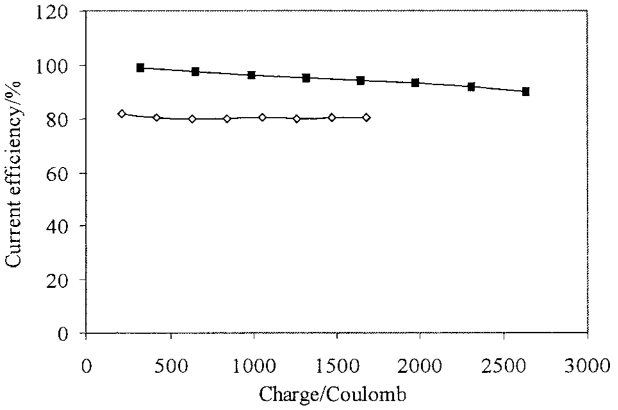

Fig. 10. Variation of current efficiencies with charge passed for flat and corrugated Nafion® 117 membranes, for runs at 1000 A m^{-2} and 0.84 dm^3 min^{-1}. Key: (■) corrugated Nafion® 117; (◇) flat Nafion® 117.

4. Conclusions

Electrohydrolysis of sodium sulfate using two geometries of Nafion® 117 cation-exchange membranes; flat and corrugated, in a two-compartment membrane electrolyses cell has been demonstrated. The effect of flow rate, current density and salt concentration on the performance of each membrane has been evaluated. The effect of electrolyte flow rate did not significantly affect the current efficiency. Productivity was greater at higher current densities; however a slight decrease in the current efficiency was observed. The salt concentration ideally should be as high as possible for EHD, since the higher salt concentration resulted in increased sodium transport number. The current efficiency was significantly improved by using corrugated membranes. In addition, improvements in transport number, sodium flux rate and achievable product concentrations were achieved with the corrugated membrane compared to the flat one. The corrugations resulted in an increase in membrane area by 57%, enabling an average improvement of approximately 15% in current efficiency for sodium hydroxide formation and an increase in the achievable base concentration of up to 77%.

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