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Dear editor

This article deals with two-compartment bipolar membrane electrodialysis and modelling. The flux rates of leakage of formate ion and sodium ion through the bipolar membrane are determined. The model gives minor and major species concentration.

Best regards

Two-compartment bipolar membrane electrodialysis for splitting of sodium formate into formic acid and sodium hydroxide: modelling

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Abstract:

The aim of this work is to model the two-compartment bipolar membrane electrodialysis for organic salts acidification. The salt studied is sodium formate which splits into formic acid and sodium hydroxide thanks to water splitting by bipolar membrane. The contamination of sodium hydroxide by formate ion is due to diffusion of molecular formic acid through the bipolar membrane and to leakage of formate ion through the same membrane under the applied current. The cation-exchange membrane does not participate to contamination of sodium hydroxide. But the leakage of hydroxide ion through the cation-exchange membrane is the major factor that influences the current efficiency of electrodialysis. The average current efficiency decreases with time principally because the sodium hydroxide leakage is desirable.

Keywords: Bipolar membrane electrodialysis, two-compartment electrodialysis, salt splitting, formic acid, modelling.

1. Introduction

Bipolar membrane electrodialysis (BMED) is used to regenerate organic acids and sodium hydroxide from sodium organic salts [1-4]. It is based on the ability of a bipolar membrane to split water into H^+ and OH^- at membrane bilayer interface. The two-compartment configuration with a cation-exchange membrane is the most widely used configuration

because it is simpler and more favourable in terms of energy than the three-compartment configuration. In the two-compartment configuration represented in Fig. 1, This Fig refers to regeneration of formic acid and sodium hydroxide from sodium formate. H^+ produced by the bipolar membrane forms formic acid with formate (almost quantitatively due to the weak acid character of formic acid pK = 3.75) while OH⁻ produced by the other face of the bipolar membrane and Na⁺ which crosses the cation-exchange membrane forms sodium hydroxide. The acid is obtained in a mixture with its salt.

The three-compartment electrodialysis was studied and modelled [5]. The mass balance of the three-compartment electrodialysis may be predicted knowing volume variations with current quantity for acid, base and salt solutions. Diffusion rates of molecular formic acid through bipolar and anion-exchange membrane and the leakage rate of hydroxide ion through the cation-exchange membrane are the model parameters. The current efficiency of formic acid production is a function of diffusion of molecular acid through the anion-exchange membrane and the bipolar membrane. Among carboxylic acids, formic acid is less studied than others like acetic or lactic acids [6,7].

Wilhem et al. [8] studied the salt ion fluxes across bipolar membranes and estimated the proportion of contaminant to 1% molar when the concentrations reach 4 mol dm⁻³. To our knowledge, no predictive model has been developed giving current efficiency for the two-compartment configuration.

Ideally, sodium hydroxide solutions obtained by two-compartment bipolar membrane electrodialysis with cation-exchange membrane is recovered pure in solution and no formate is present. However, this is not the case. Some formate pollutes the sodium hydroxide solution and this may be undesired.

Carboxylic acids diffusion was mentioned as one factor reducing the current efficiency. Koter S. [9] studied the weak acids production. The modelling given is very complex. Except [5, 10], literature is poor concerning the conversion of sodium formate into formic acid and sodium hydroxide by bipolar membrane electrodialysis.

The performance of an electromembrane process is given in term of current efficiency which represents the ratio of the mole number produced or transferred and the number of faradays passed through the system. The integral or average current efficiency (ICE) between time 0 and time t is defined by the relation:

$$ICE_{0,t} = \frac{\Delta N}{iAt / F} \tag{1}$$

where ΔN is the variation of mole number of the component between time 0 and time t, i the current density constant during time t, A is the membrane area, F is the faraday constant $(96485 \text{ A s mol}^{-1} = 26.8 \text{ Ah mol}^{-1})$ The differential current efficiency (DCE) is defined as: $DCE_t = \frac{dN}{iAdt/F}$

The aim of this study is to model the functioning of the two-compartment bipolar membrane electrodialysis configuration. It is also to identify the contamination of sodium hydroxide by formate ion and the factors limiting the current efficiency of formic acid production.

(2)

2. Experimental details

2.1. Experimental set-up

CMB cation exchange membrane and BP-1 bipolar membrane were used. These membranes were supplied by Eurodia Industries. Electrodialysis was performed with a cell stack EUR 2B-BIP supplied by the same company. It was composed of 6 cells with two-compartments (Fig. 1). The active area of each cell was 2 dm^2 . Two nickel electrodes with NaOH 2 mol dm⁻³ rinsing solution terminated the stack. They did not interfere with the electrodialysis. Temperature was measured but not controlled (average temperature has been taken). A constant current was applied. The circulation of solutions in the cell was started 5 to 10 min before the current was switched on.

The experiments of diffusion of formic acid from a mixture of formic acid sodium formate were done as described in a previous paper [5].

2.2. Reagents and solutions:

Sodium formate 98% and sodium hydroxide 37% were supplied by VWR.

Initial concentration of sodium formate solution was about 2 mol dm⁻³ and initial concentration of sodium hydroxide was about 0.5 to 1 mol dm⁻³. The volume of both solutions was 1 to 2 dm^3 for 6 cells

These solutions were titrated for acid and base contents. Formate (as formic acid or sodium formate) and sodium ion in low concentration were determined using ionic chromatography (Dionex).

1 2 3

3. Results and discussion

The model proposed describes the functioning of a two-compartment bipolar membrane electrodialysis with a cation-exchange membrane in alternation with bipolar membrane. The model is able to describe the contamination of sodium hydroxide solution by formate and to give the mass-balance of the electrodialyser.

3.1. Modelling

The subscripts a and b refer to acid/salt and sodium hydroxide solutions respectively. According to Fig. 1, formic acid may diffuse through bipolar membrane into sodium hydroxide solutions. Also, leakage of formiate ion through the bipolar membrane participates to contamination of sodium hydroxide solution. The transfer of formate ion through the cation-exchange membrane is unlikely due to migration. Fig. 1 summarises the exchange of species in the electrodialysis device. Some fluxes are desired (sodium from salt compartment to base compartment, H^+ and OH^- from the bipolar membrane to acid/salt and base compartment respectively). The others are undesired.

3.1.1. Model assumptions

To model the two-compartment bipolar membrane electrodialysis the following assumptions are made:

Assumption 1: Hydroxide ion migration (leakage) through the cation-exchange membrane is observed. It is the same than for the three-compartment configuration. It depends only on sodium hydroxide solution concentration, on temperature and on the membrane. The hydroxide leakage flux rate is noted h. The number of moles of hydroxide ion N_{OH} crossing the unit area of cation-exchange membrane during an unit of time is $N_{OH} = hi[NaOH]_b$ where [NaOH]_b is the concentration of sodium hydroxide in base compartment.

Assumption 2: diffusion of formate ion through the cation-exchange membrane is negligible because migration is the major effect. Without current diffusion of formate ion through the cation-exchange membrane occurs. The diffusion of molecular acid through the cation-exchange membrane is counteracted by sodium hydroxide ion leakage. Due to the passage of hydroxide ion through this membrane, reaction of formic acid with sodium hydroxide occurs in the membrane or in the boundary layers. This leads to formate ion which migrates towards the anode making an U-turn. So, diffusion of formate ion through the cation exchange membrane does not occur during electrodialysis.

Assumption 3: The formic acid diffusion through the bipolar membrane is proportional to acid concentration. This will be checked.

3.1.2. Diffusion and migration

For diffusion of neutral species through surface A of solution-membrane the number of moles crossing A during a time dt, is written:

$$dN = -D_m A \frac{d[X]}{dx} dt \tag{3}$$

x is the direction perpendicular to the membrane and D_m is the diffusion coefficient of X in the solution or in the membrane.

The concentration of X in solution and the boundary layers is constant since an increase of mixing had no effect. The concentration in the receiving solution is very low and could be taken equal to zero. Thus the concentration difference in the membrane is nearly [X]. The diffusion number of moles may be written:

$$dN = -\frac{D}{e}A[X]dt \tag{4}$$

Where D is the diffusion coefficient in the membrane and e is the thickness of the membrane. For diffusion and migration the number of moles crossing A during a time dt is given by Nernst-Planck equation:

$$dN = -DA(\frac{d[X]}{dx} + [X]z_X \frac{d\phi}{dx})dt$$
(5)

where z_X is the charge of X and ϕ is the electrical potential. If the migration takes place alone the flux is proportional to the concentration [X] and proportional to the current.

Diffusion or migration of a species X is proportional to X concentration in the solution from which it diffuses or migrates, to surface area of membrane and duration of diffusion or migration considered. The mole number dN of species X (diffusion: dN_{dif} , migration: dN_{mig} ,) is written:

$$dN_{dif} = k_{dif} A[X] dt$$
(6)

$$dN_{\rm mig} = k_{\rm mig} i A[X] dt \tag{7}$$

 k_{dif} and k_{mig} are the flux rates with: $k_{dif} = k_{mig} = .D/e$

3.1.3. Mass balance of the cell stack

The mass-balance is written taking into account:

- The migration of formate ion through the bipolar membrane (leakage)

- The migration of sodium ion through the bipolar membrane (leakage)

Thus the number of moles of H^+ and OH^- produced by the bipolar membrane (surface A) during time dt is given by:

$$dn_{H^{+}} = dn_{OH^{-}} = \frac{iA}{F}dt - dn_{formate} - dn_{Na^{+}}$$
(8)

This is because the current is transported by all ions (the total current density being i) If f and g are the flux rates for leakage of formate ion and sodium ion respectively, then:

$$dn_{formate} = fiA[HCOO^{-}]_{a}dt \tag{9}$$

and

$$dn_{Na+} = giA[Na^+]_b dt \tag{10}$$

The acid balance is the following:

$$d(V_a[HCOOH]_a) = (\frac{iA}{F} - fiA[HCOO^-]_a - giA[Na^+]_b - k_{bip}A[HCOOH]_a - hiA[OH^-]_b)dt$$
(11)

The flux rate of diffusion of formic acid through the bipolar membrane has been determined [5]: $k_{bip} = 0.0045$ to 0.005 dm h⁻¹ at 298 K with an activation energy of 18 kJ mol⁻¹. The value of flux rate of leakage of hydroxide anion through the cation exchange membrane is h = 0.0032 dm³ Ah⁻¹ at 298K. The activation energy is estimated to 23 kJ mol⁻¹. This equation expresses that the acid accumulation is equal to the number of moles of H⁺ produced minus the acid lost by diffusion from compartment a to compartment b and the acid which reacts with the leaked hydroxide ions.

The salt balance is given by the equation:

$$d(V_{a}[HCOO^{-}]_{a}) = -dn_{H^{+}} - fiA[HCOO^{-}]_{a}dt + hiA[OH^{-}]_{b}dt = (-\frac{iA}{F} + giA[Na^{+}]_{b} + hiA[OH^{-}]_{b})dt$$
(12)

Leakage of formate ion through the bipolar membrane does not appear formally in this equation because its transport takes part in total current passage iAdt/F.

The hydroxide ion balance gives:

$$d(V_{b}[OH^{-}]_{b}) = dn_{OH^{-}} - (hiA[OH^{-}]_{b} + k_{bip}A[HCOOH]_{a})dt = (\frac{iA}{F} - fiA[HCOO^{-}]_{a} - giA[Na^{+}]_{b} - hiA[OH^{-}]_{b} - k_{bip}A[HCOOH]_{a})dt$$
(13)

Formate ion (contaminant) in sodium hydroxide solution is given by the following equation:

$$d(V_b[HCOO-]_b) = (k_{bip}A[HCOOH]_a + fiA[HCOO^-]_a)dt$$
(14)

The first member of equations 11 to 14 is the differentiation of the product of a volume and a concentration both function of time. Hence:

$$d(V[X]) = Vd[X] + [X]dV$$
(15)

The volume variations are linear versus time and versus the current [11].

$$dV_a = aiAdt \text{ et } dV_b = biAdt$$
(16)

a and b are determined experimentally.

3.2. Application of the model

In order to test this model, the experimental data obtained during electrodialysis experiments were fitted to equations 11 to 16. The calculation is done as follows: the initial conditions are stated. Then the calculation is undertaken for dt increment: The elemental variations $d[HCOOH]_a$, $d[HCOO^-]_a$, $d[OH^-]_b$ are calculated using equations 11 - 15 and using the previous values for the concentrations $[HCOOH]_a$, $[HCOO^-]_a$ and $[OH^-]_b$. Then the actual values for $[HCOOH]_a$, $[HCOO^-]_a$ and $[OH^-]_b$ are obtained. The concentration of formate ion in sodium hydroxide $[HCOO^-]_b$ is computed also (equation 15)

3.2.1 Volume variations

Fig. 2 reports variations of specific volumes of the two solutions versus specific current quantity (quantity of electricity per an unit of area surface). Different experiments are considered in Fig. 2 included different current densities. The variations are linear Acid/salt solution: $\Delta V_a = aiAt$ with $a = -3.1 \ 10^{-3} \ dm^3 \ Ah^{-1}$ Base solution: $\Delta V_b = biAt$ with $b = 2.1 \ 10^{-3} \ dm^3 \ Ah^{-1}$

These volume variations are essentially due to water transfer by electroosmosis.

3.2.2 Sodium transfer through the bipolar membrane

The sodium ion transfer from base solution to acid/salt solution through the bipolar membrane can not be measured in the two compartment configuration because of the presence of sodium

ion in the receiving solution. This study was done with the three-compartment configuration. The leakage of sodium is quite the same in the two configurations. Sodium ion was determined in acid compartment. Fig. 3 shows the variations of mole number of sodium in the acid compartment versus time for an experiment where sodium hydroxide solution and sodium formate solution are renewed. For sodium hydroxide concentration between 1 and 3 mol dm⁻³ (average value 2 mol dm⁻³) and a current density of 5 A dm⁻² it is found that: $\frac{dN_{Na^+}}{dM_{Na^+}} = 210^{-4} \, mol. dm^{-2}.h^{-1}$ (17)

$$\frac{dN_{Na^{+}}}{Adt} = 210^{-4} \, mol.dm^{-2}.h^{-1}$$

$$dN_{Na^{+}} = giA[\overline{NaOH}]_{b}dt$$
(17)
(17)
(17)

Where $[\overline{NaOH}]_{h}$ is the average concentration of sodium hydroxide solution.

This permits the calculation of the sodium ion flux rate of leakage through the bipolar membrane. The magnitude of the value of the flux rate g may be calculated $g \approx 2 \ 10^{-5} \ dm^3 \ Ah^{-1}$.

3.2.3 Fitting of formate in sodium hydroxide

Before starting, a non-negligible concentration of formate is detected in sodium hydroxide solution. This is probably due to diffusion of sodium formate when no current is applied. It is better to limit the contact between solutions when the current is switched off. The mole number of formate crossing the membranes between time 0 and time t, N_{F-} , is calculated from the concentrations and the volumes at these moments.

$$N_{F} = \frac{V_{b}(t)}{A} [HCOO]_{b} - N_{F0} = \frac{V_{b}(t)}{A} [HCOO]_{b} - \frac{V_{b}(0)}{A} [HCOO]_{b0}$$
(18)

where $[HCOO]_{b0}$ and $V_b(0)$ are respectively the concentration of formate in sodium hydroxide solution and the volume of this solution at t = 0.

Fig. 4 reports the variations of the mole number of formate crossing the unit area of bipolar membrane versus time. The experimental points are drawn (calculated by equation.18 with an interval of error estimated to 10%). The average temperature is near 300 K. Several experiments were made. Not all are reported here. The experiments show that the current density has an effect on the passage of formate: the higher the current density the higher the flux through membranes. The curve fitting is done by the method of least squares. It leads to the following value of the flux rate $f = (2.2 \pm 0.2) 10^{-4} \text{ dm}^3 \text{ Ah}^{-1}$. The value of the flux rate of leakage of sodium ion through the bipolar membrane, g, is about 2 10⁻⁵ dm³ Ah⁻¹ but this small value has no effect on the passage of formate through the membrane. The low

dispersion of *f* values shows that the model describes well the contamination of sodium hydroxide solution by formate ion. Thus, the assumptions made are validated. The bipolar membrane is the only responsible of contamination of sodium hydroxide solution The contribution of formate migration through the bipolar membrane is obtained by comparing the flux of formate during time dt i.e. $fi[HCOO^{-}]_a$ to the total flux through the membrane (i/F). The value θ of the transport number of formate ion is equal to:

$$\theta = fF[HCOO^{-}]_{a} = 0.006[HCOO^{-}]_{a} \tag{19}$$

The highest value corresponds to the beginning of the operation generally at 2 mol dm⁻³. Thus the maximum value for transport number of formate ion through the bipolar membrane is near 1 %. This is in agreement with the known results [8].

3.2.4 Diffusion of formic acid from acid/salt solutions through bipolar membrane

Diffusion through the bipolar membrane for mixtures of formic acid and sodium formate was measured. The total concentration of formate (formic acid or formate ion forms) was fixed to 2 mol dm⁻³. The receiving phase was sodium hydroxide solution 1 mol dm⁻³. Fig. 5 reports the variations of formate flux through the bipolar membrane vs. the concentration of formic acid. At concentration of acid equal to 0 diffusion of 2 mol dm⁻³ formate ion solution is observed. The flux of diffusion increases as the acid concentration increases. Deviation from linearity is observed. Diffusion of formate ion is decreasing from its initial value to zero for the 2 mol dm⁻³ formic acid solution. This means that the mixture does not behave ideally. But the deviation is small and may be neglected in a first step.

The diffusion flux of formic acid is then nearly proportional to the acid concentration. The diffusion of formate ion does not occur when the current is switched on as seen before.

3.2.5. Fitting of variations of acid, base and salt

The experimental variations of concentrations of formic acid, sodium formate and sodium hydroxide are confronted to the curves determined by the model. Fig. 6 reports an example of results. The agreement is remarkable. The current efficiencies for production of acid and base and for consumption of sodium formate may be predicted by the model. The average current efficiency between time 0 and time t (as defined by equation 1) decreases with time. This is due in part to diffusion of molecular acid through the bipolar membrane which increases when the acid concentration increases. The major factor that decreases the current efficiency is the leakage of hydroxide ion. During the experiment, the base concentration increases and

 consequently the leakage. This explains the variations of current efficiency during the experiment. Fig. 7 reports the variations of current efficiency during an experiment of electrodialysis. The error on current efficiency is estimated to 3%. Experimental points are in accordance with calculated values. This is in favour of the assumption of proportionality of leakage flux of hydroxide ion to the concentration of sodium hydroxide. The current density has only a little effect on variations of current efficiency. To obtain high current efficiency, one has to limit the concentration of sodium hydroxide. Only a slight decrease should be obtained if this concentration is maintained constant. An increase of the volume of sodium hydroxide solution is favourable as could be seen in Table 1 which gives calculated current efficiencies versus the specific initial volume of sodium hydroxide solution.

4. Conclusion

The two-compartment configuration with a cation-exchange membrane is widely used in the acidification of organic salts. This is because it is simpler and more favourable in term of energy consumption than the three-compartment configuration.

The contamination of sodium hydroxide solution by formate is due to:

- diffusion of molecular formic acid through the bipolar membrane

- leakage (migration) of formate ion through the bipolar membrane

The cation-exchange membrane is not concerned as far as contamination is considered.

The contribution of diffusion of formic acid and leakage of formate ion through the bipolar membrane to current efficiency is small. The current efficiency is principally defined by the leakage of hydroxide ion through cation-exchange membrane. During the electrodialysis, the current efficiency decreases as time increases. This may be explained by the increase of sodium hydroxide concentration, which means an increase of leakage of hydroxide ion.

The leakage of formate ion through the bipolar membrane is proportional to current density and to sodium hydroxide concentration. The values of flux rate of leakage of formate ion are given in Table 2, which recapitulates all the flux rates of interest in modelling of a twocompartment bipolar membrane electrodialysis of sodium formate. Note that the flux of leakage of formate is not to consider for the three-compartment configuration because the formate in the acid compartment is under acid form and the formate ion concentration is very small [12].

To maintain a high current efficiency, the sodium hydroxide concentration should be low but an optimal value must be used since too low concentration of sodium hydroxide will be energetically unfavourable. References

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Fig. 1: Two-compartment BMED principle and the fluxes through the membranes (dashed arrows: undesirable flux, continuous arrows: desirable flux)

Fig. 2: Volume variations for the acid circuit (negative values) and for the base circuit (positive values) vs. current quantity for current densities $2.5-5-7.5-10 \text{ A dm}^{-2}$

Fig. 3: Formic acid contamination by sodium ion in the three-compartment experiment, base and salt solutions renewed (average concentration of base 2 mol dm⁻³, i = 5.00 A dm⁻², T = 303 K)

Fig. 4: Specific formate mol number crossing the membrane vs. time, T = 300 K

initial specific volume of salt (base) 0.14 dm (0.08 dm), concentration of salt (base) 1.84 mol dm⁻³ (0.90 mol dm⁻³), i = 9.95 A dm⁻²; \diamond initial volume of salt (base) 0.14 dm (0.09 dm); concentration of salt (base) 1.87 mol dm⁻³ (0.85 mol dm⁻³), i = 7.50 A dm⁻²; Δ initial volume of salt (base) 0.16 dm (0.12 dm); concentration of salt (base) 1.81 mol dm⁻³ (0.97 mol dm⁻³), i = 5.00 A dm⁻²; **a** initial volume of salt (base) 0.16 dm (0.09 dm); concentration of salt (base) 1.84 mol dm⁻³ (0.86 mol dm⁻³), i = 2.50 A dm⁻²

Fig. 5: Diffusion from acid/salt mixtures through BP1 membrane ([HCOOH] + [NaHCOO] = 2 mol dm^{-3} , T = 298 K)

Fig. 6: Mass balance of major products in BMED vs. time, \blacksquare formic acid, \blacklozenge sodium formate, Δ sodium hydroxide

Fig. 7: Average current efficiency vs. time, experimental points and fitted curve. Initial specific volume of salt (base) 0.14 dm (0.08 dm), concentration of salt (base) 1.84 mol dm⁻³ (0.90 mol dm⁻³), T = 300K, i = 9.95 A dm⁻²

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Lit of tables

Table 1: Current efficiency vs. specific initial volume of sodium hydroxide solution, specific initial volume of salt 0.14 dm, concentration of salt (base) 1.84 mol dm⁻³ (0.90 mol dm⁻³), T = 300 K, i = 9.95 A dm⁻²

Table 2: Values of flux rates of different transfers occurring in the two-compartment configuration during bipolar membrane electrodialysis of sodium formate.

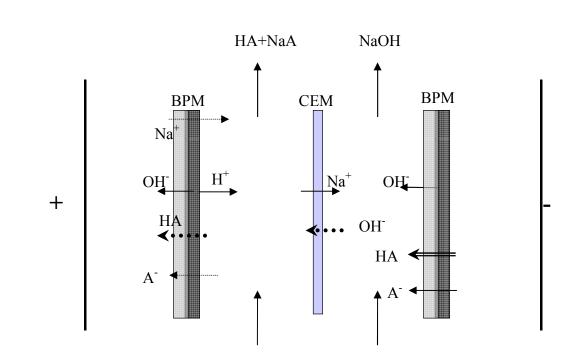


Fig. 1

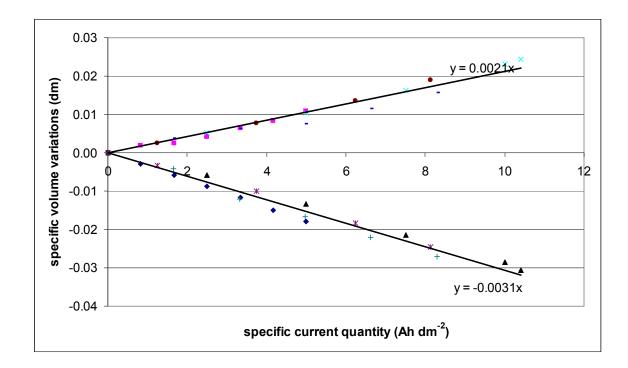


Fig.2

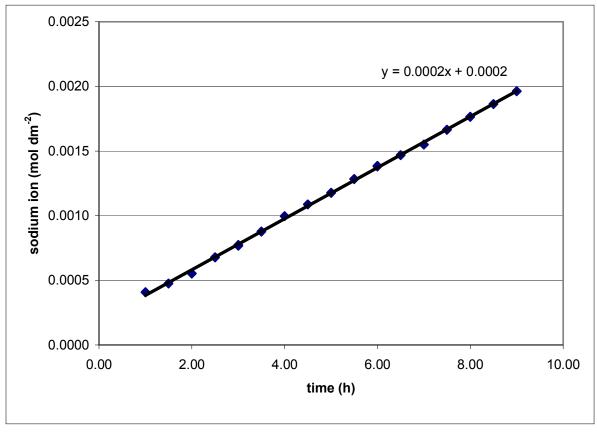


Fig. 3

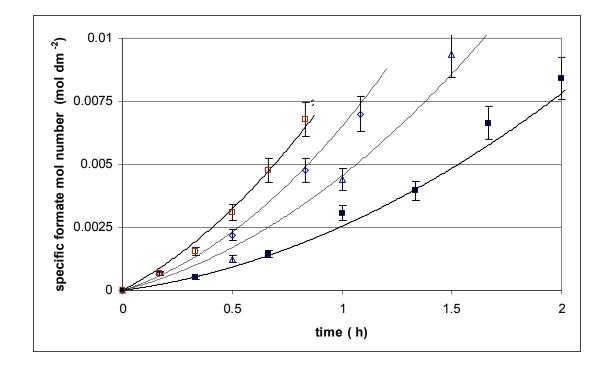
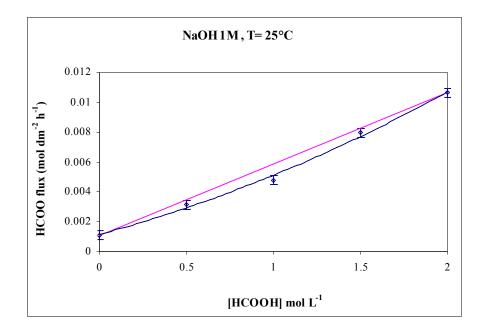
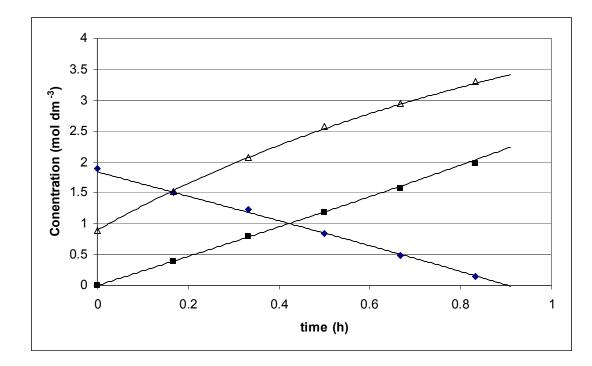


Fig. 4









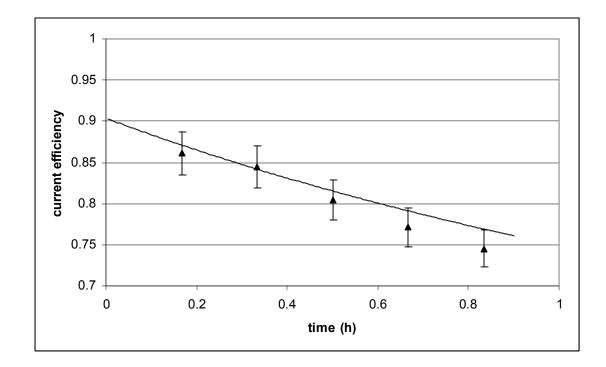


Fig. 7:

Table 1:

Specific volume of sodium	Current efficiency	
hydroxide solution (dm)		
0.1	0.79	
0.2	0.84	
0.5	0.87	

Table 2:

Flux rates	Values	Study
Diffusion of molecular formic	4.5 to 5.0 10^{-3} dm h ⁻¹ at 298	Three-compartment
acid through the bipolar	K*	electrodialysis [5]
membrane		
Hydroxide ion leakage through	$3,2 \ 10^{-3} \ dm^3 \ Ah^{-1} \ at \ 298 K^{**}$	Three-compartment
the cation-exchange membrane		electrodialysis [5]
Formate ion leakage through the	$2,2 \ 10^{-4} \ dm^3 \ Ah^{-1} \ at \ 300 \ K$	This study
bipolar membrane		
Sodium ion leakage through the	$2 \ 10^{-5} \ dm^3 \ Ah^{-1} \ at \ 298K$	Three-compartment
bipolar membrane		electrodialysis [5] and this
		study
Volume variations of acid/salt	$3.1 \ 10^{-3} \ dm^3 \ Ah^{-1}$	This study
compartment		
Volume variations of base	$2.1 \ 10^{-3} \ dm^3 \ Ah^{-1}$	This study
compartment		
+ + · · · · · · · · · · · · · · · · · ·		

*Activation energy: 18 kJ mol⁻¹

**Activation energy: 23 kJ mol⁻¹