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Ion transport in a two membrane electrowinning cell for the production of hydrochloric acid

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A three-compartment electrowinning cell has been evaluated for the regeneration of HCl from metal chloride catholyte. By segregating the catholyte with an anion exchange membrane, and the anolyte with a cation exchange membrane from the middle electrolyte(ampholyte) compartment, HCl could be produced in the ampholyte electrochemically up to one molality. The anolyte consisted of sulphuric acid. Successful operation of such a double membrane cell depends on controlling ion transport through the membrane, especially chloride migration into the anolyte. Results of electrowinning and self-diffusion experiments for three types of cation exchange membrane are presented and discussed.

1. Introduction

The final step in base metal hydrometallurgy is to obtain the metal from a purified pregnant solution. The most common method is electrowinning since it recovers the lixiviants and allows (near)closed circuit operation. In the industrial process of nickel chloride electrowinning, for instance, metal is deposited at the cathode and chlorine is evolved at the anode. The byproduct chlorine can be used directly for the leaching of metal bearing sulphides or alloys, but for oxides hydrochloric acid is preferred. In such cases, chlorine must be converted into hydrochloric acid by burning the chlorine with hydrogen. The collection of chlorine during the electrowinning requires a complex, reliable system. It complicates the tankhouse design and operation. In addition, the production of chlorine, followed by conversion of chlorine into hydrochloric acid increases process costs. Hence the direct electrolytic regeneration of chloride in the form of HCl should be given serious consideration[1].

In previous work[2], the possibility of using a membrane cell for the regeneration of chloride in the form of HCl has been investigated. It was found, not surprisingly, that a decrease of the pH in the catholyte resulted in a low cathodic current efficiency and a poor quality of nickel deposition in a single cation exchange membrane cell. In a two membrane cell, a relatively stable pH in the catholyte and a low chloride concentration in the anolyte could be maintained. A two membrane cell with a similar configuration was used in the electrolysis of sodium sulphate[3]. Another type of double membrane electrolytic cell was also adopted in the production of high purity cobalt and nickel from superalloy scrap[4]. Neither approach was aimed at regenerating hydrochloric acid. A variant by which the two membrane cell unit can be integrated in a process is illustrated in Fig. 1.

2. Experimental details

In this work, the composition changes of the anolyte, the ampholyte* and the catholyte were recorded as function of time to study the ion transport in the two membrane cell. The performance of three types of cation exchange membrane in the two membrane cell has also been studied. The experiments were carried out with and without an applied potential difference over the cell, referred to as electrowinning experiments and self diffusion experiments, respectively, in order to investigate the influence of the electric potential on ion transport in the two membrane cell. Finally, the possibility of using the two membrane cell to regenerate chloride in the form of HCl is discussed.

All experiments were carried out in a cell built of Perspex, which consisted of three compartments of equal dimensions clamped together with external tie rods and separated by one piece of cation exchange membrane and one piece of anion exchange membrane, schematically shown in Fig. 2. The compartment between the anode compartment and cathode compartment is named the ampholyte compartment

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* The name 'ampholyte' is being suggested to denote the electrolyte of the middle compartment. *Amphi* = (from) both sides.

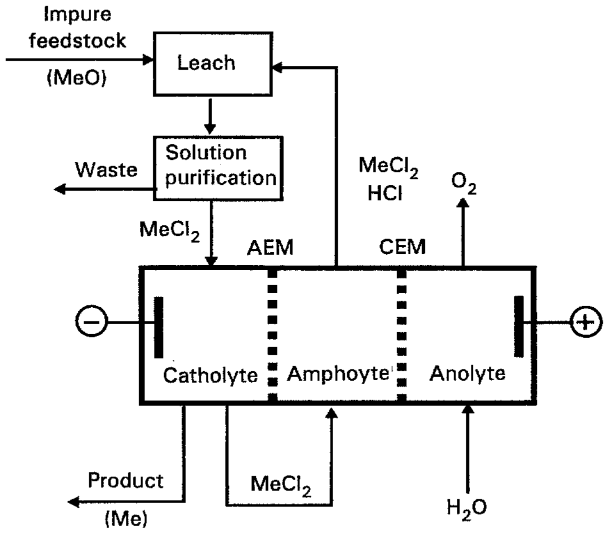

Fig. 1. One process variant by which the two membrane cell could be utilized.

after the electrolyte. The solution content of each compartment was 1000 ml and the effective dimensions of the membrane was 10 cm × 10 cm. Three different types of cation exchange membrane listed in Table 1 were used, in combination with the Neosepta ACM anion exchange membrane.

Both the electrowinning and diffusion experiments were conducted at 50 °C. The temperature was maintained by operating the cell in a water bath equipped with Thermomix-1480 (Braun Melsungen AG). In the electrowinning experiment, a potentiostat with the software CMS100 (Gamry Instruments Inc.) was used to supply a constant current and to measure the electrode potential. A saturated calomel electrode was used as the reference electrode, hence all potentials in this paper are relative to the saturated calomel electrode (SCE). A lead–antimony (10% Sb) plate was adopted as the anode in all electrowinning experiments. A dimensionally stable anode (DSA®) was tested in the later stages of the electrowinning experiments to compare the cell voltage with that of the lead-antimony anode. The cathode was a plate of pure nickel. The effective surface area of the anode and the cathode were both 30 cm^2. The electrowinning experiments were operated at a current density of 200 A m^{-2} and 1.0 M NiCl$_2$ solution was used as the catholyte. Since the ampholyte consists of spent catholyte, 0.2 M NiCl$_2$ was arbitrarily selected as the initial ampholyte and 1.0 M H$_2$SO$_4$ was used as the anolyte. The cell voltage was measured by connecting a voltmeter to the anode and the cathode in the two membrane cell. The cathodic current efficiency was determined by weighing the cathode before and after the electrowinning experiment. All experiments were conducted batchwise.

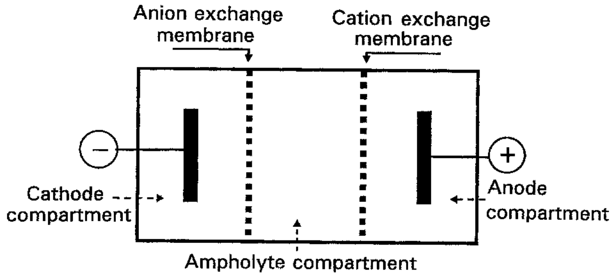

Fig. 2. Schematic cross section of the two membrane electrolytic cell.

The chloride concentration in the anolyte was measured with an ion selective electrode (IS-CL Chloride electrode, Unicam). The chloride concentration in the catholyte and the ampholyte was measured by titration with silver nitrate using dichlorofluorescein as the indicator. The nickel concentration was measured by atomic absorption spectrophotometry (Perkin–Elmer-AA275). The acidity of the anolyte and the ampholyte was measured by titration with sodium hydroxide.

All chemicals were analytical grade from Merck Co., Ltd. The solutions were prepared by dissolving salt or diluting acid in distilled deionized water.

3. Results and discussion

3.1. *Electrowinning parameters with the two membrane cell*

The operating results of nickel chloride electrowinning for the two membrane cell are shown in the Table 2.

It can be seen from Table 2 that the current efficiency and the voltage drop over the membranes and electrolytes are within an acceptable range. The voltage drop was obtained by subtracting the anodic potential and cathodic potential from the total cell voltage. When lead–antimony was adopted as the anode, the cell voltage was higher than that in the industrial nickel chloride electrowinning process [5], but when a DSA® was used as the anode a similar cell voltage was obtained. At the same time, the cell voltage with the lead-antimony anode was still in the range of cell voltage measured on a nickel sulphate bath, namely 3.5 V at a current density of 183 A m^{-2} [6]. A smooth and compact nickel deposit was obtained on the cathode in all experiments.

3.2. *Ion transport in the two membrane cell during the electrowinning experiments*

In the electrowinning experiments, the current is carried by the ions which cross the membrane. In the two membrane cell, the ampholyte is separated from the anolyte by a cation exchange membrane(CEM), and from the catholyte by an anion exchange membrane(AEM) as shown in Fig. 3. During the electrowinning of nickel chloride, only protons are expected to migrate from the anolyte to the ampholyte. Chloride ions are expected to migrate from the catholyte to the ampholyte, hence the electric current through the cation exchange membrane is carried mainly by protons, and by chlorides through the anion exchange membrane. However, diffusion of nickel caused by the concentration gradient of nickel between the anolyte and the ampholyte is unavoidable. The ion

Table 1. Membranes investigated

Name	*Nafion®-117*	*Nafion®-350*	*Flemion®*	*Neosepta–ACM*
Type	H^+	H^+	H^+	Cl^-
*Electric resistance/Ω cm^2	1.5	4.8	1.4	4.0–5.0
†Exchange capacity/mequiv g^{-1}	1.1	1.5	1.1	1.5–2.0
Thickness/μm	140	250	100	110–130
Reinforcing	no	yes	no	yes

* Electric resistance: Equilibrated with 0.5 N NaCl solution, at 25 °C.
† Exchange capacity/meq g^{-1}. Na-form (or Cl-form) dry membrane.

Table 2. Test conditions and results for nickel chloride electrowinning in the two-membrane cell

Type of membrane	*Nafion®-117*	*Nafion®-350*	*Flemion®*
Current density/A m^{-2}		200	
Electrolyte temperature/°C		50	
Cathodic potential/V		−0.71	
Anodic potential with Pb–Sb/V		1.85	
Anodic potential with DSA/V		1.35	
Cell voltage with Pb–Sb anode/V	3.15	3.10	3.15
Cell voltage with DSA/V	2.71	2.65	2.75
Voltage drop over membranes and electrolytes/V	0.65	0.60	0.65
Cathodic current efficiency/%	96	97	96

transport through the membranes can be deduced from the change of ion concentrations in three electrolytes.

3.2.1. Ampholyte. Protons can be expected to be the most important electric current carrier through the cation exchange membrane. This is confirmed by the acidity change in the ampholyte during nickel chloride electrowinning as shown in Fig. 4. The acidity increase for the three types of membrane is similar.

Because of the concentration gradient of nickel between the ampholyte and the anolyte, diffusion of nickel ions from the ampholyte to the anolyte through cation exchange membrane(CEM) is to be expected, though it is counteracted by the positive potential at the anode. The nickel concentration in the ampholyte decreased as shown in Fig. 5, in the same three electrowinning experiments as shown in Fig. 4.

Because the catholyte was separated from the ampholyte by an anion exchange membrane, the electric current between the catholyte and the ampholyte can only be realized by the transport of anions (i.e., chloride ions). The chloride concentration in the ampholyte reasonably increased partly by ionic migration and partly by diffusion as shown in Fig. 6.

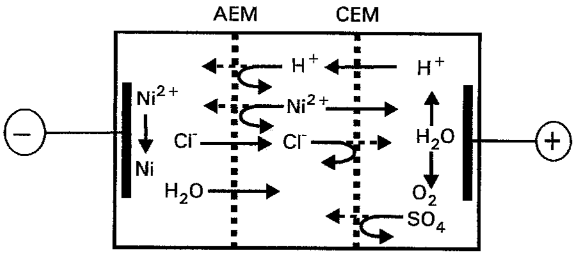

Fig. 3. Simplified diagram. (Nonhydrated ion and water transport in the two membrane cell during the electrowinning of nickel chloride).

From Figs 4 and 6, it can be seen that both the acidity and the chloride concentration in the ampholyte increased with time. Hydrochloric acid is formed.

3.2.2. Catholyte. The nickel concentration in the catholyte decreased linearly with time due to the deposition of nickel at the cathode during the electrowinning experiment. The nickel concentration change shown in Fig. 7 corresponds to a current efficiency of more than 95%. During the deposition of nickel, the surplus of chloride present in the catholyte migrates or diffuses to the ampholyte to maintain charge balance and transport the current. The decrease in chloride concentration, as shown in Fig. 8, is in stoichiometric agreement with the nickel deposition shown in Fig. 7.

3.2.3. Anolyte. The main purpose of using the two membrane cells is to maintain a low chloride concentration in the anolyte to obtain evolution of oxygen instead of chlorine at a lead–antimony anode, or alternatively, for the oxidation of reducing agents such as methanol, hydrogen gas etc. on a platinum type electrode. Hence a low chloride concentration in the anolyte is critical for either mode of operation. A cation exchange membrane set between the anolyte and the ampholyte was expected to prevent chloride transport from the ampholyte to the anolyte. Unfortunately, a small amount of chloride leakage to the anolyte must be expected. The leakage of chloride through the three types of cation exchange membrane is quite different, as shown in Fig. 9. The chloride leakage rate through Nafion®-350 membrane is only one fifth of that in Nafion®-117 membrane and one seventh of that in Flemion® membrane. This is consistent with Nafion®-350 in being designed for improved anion rejection [7].

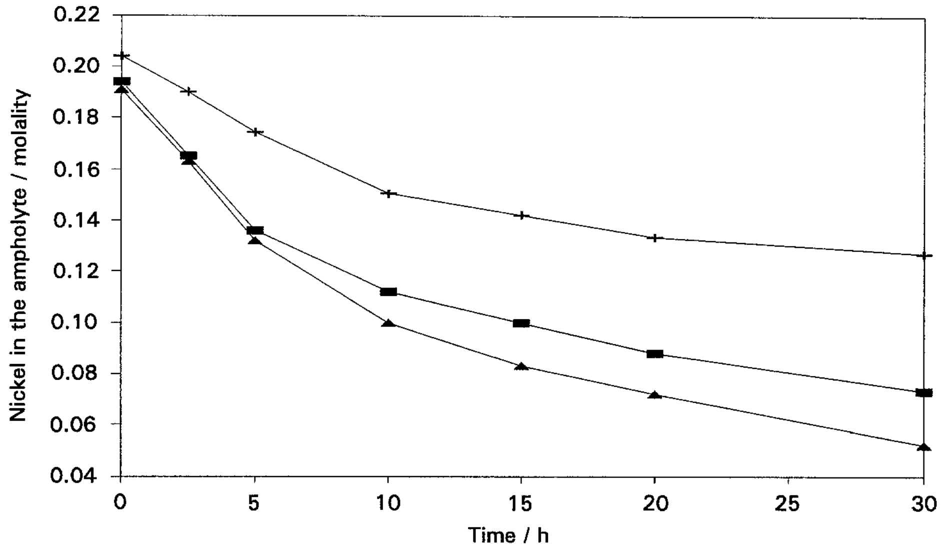

Fig. 4. Nickel concentration of the ampholyte as function of time when electrowinning nickel chloride. Key: (■) Nafion®-117; (+) Nafion®-350; (▲) Flemion®.

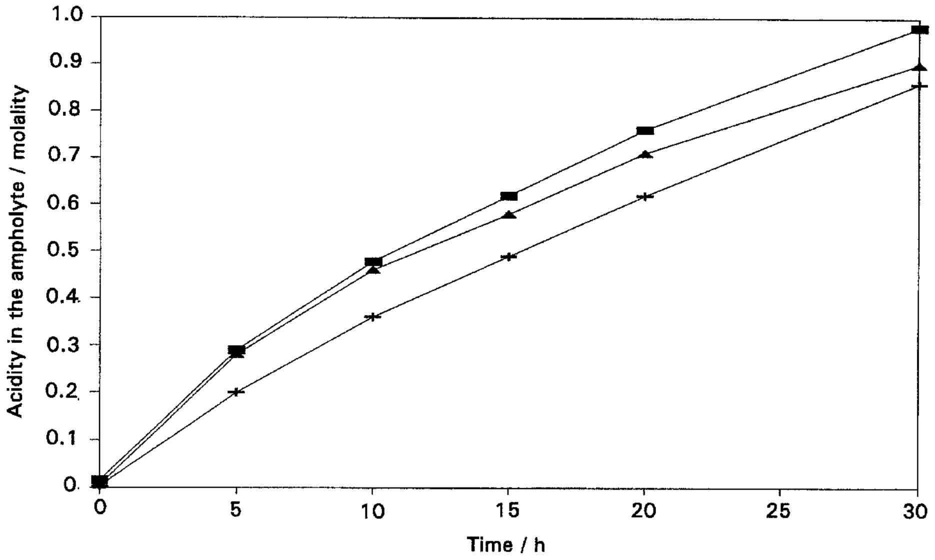

Fig. 5. The acidity of the ampholyte as function of time when electrowinning nickel chloride. Key: see Fig. 4.

3.3. *Ion transport in the two membrane cell during diffusion experiments*

In the electrowinning experiment, because the leakage of chloride ions into the anolyte is in the same direction as the electric field, it is not totally surprising that a small amount of chloride migrates through the cation exchange membrane between the anolyte and the ampholyte. It was expected that a lower chloride concentration would be obtained in the anolyte when no electrical potential is applied over the membrane cell. For this reason, some experiments with

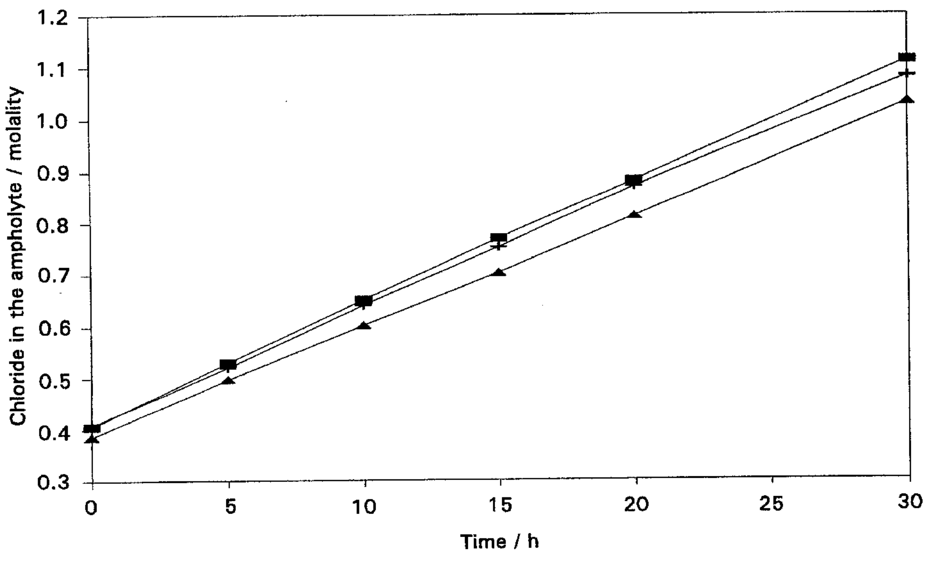

Fig. 6. Chloride concentration in the ampholyte as function of time in the electrowinning of nickel chloride. Key: see Fig. 4.

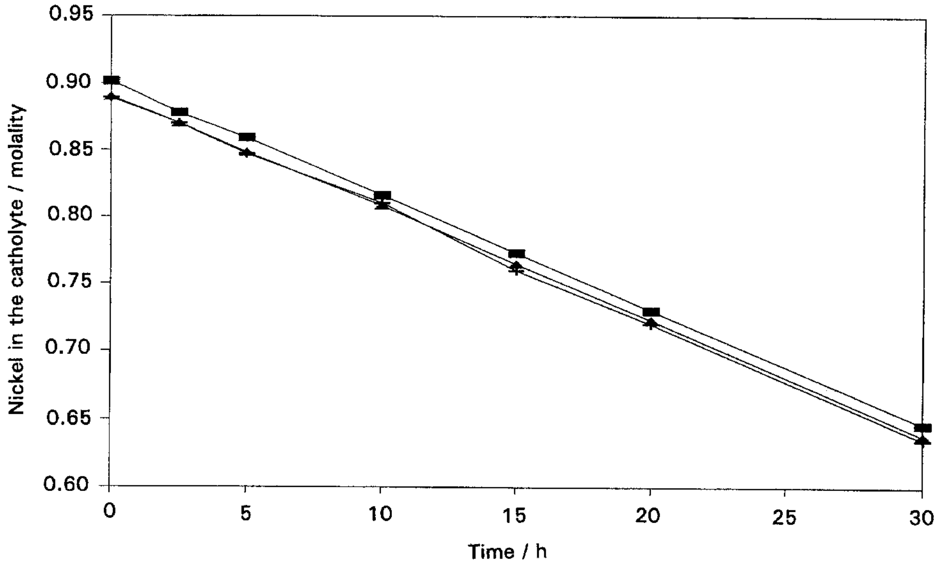

Fig. 7. Nickel concentration in the catholyte as function of time when electrowinning nickel chloride. Key: see Fig. 4.

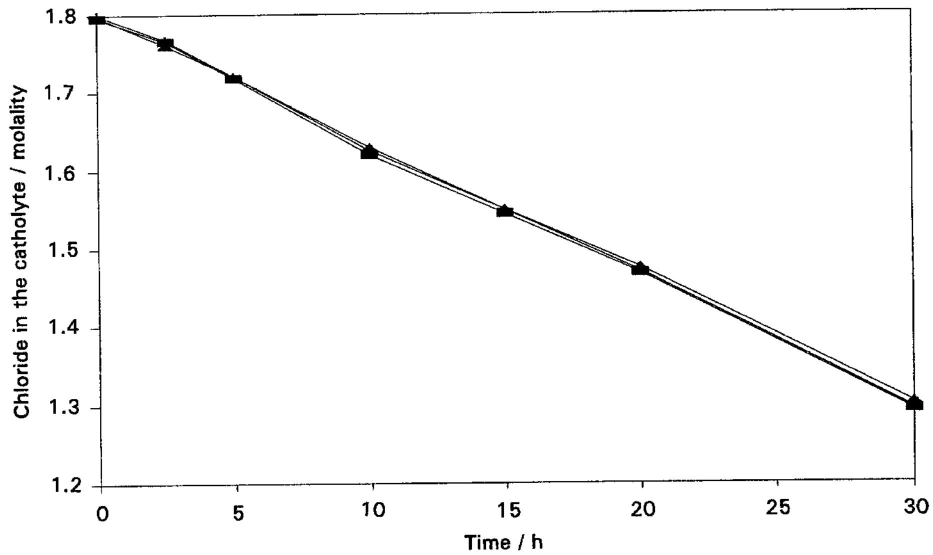

Fig. 8. Chloride concentration in the catholyte as function of time when electrowinning nickel chloride. Key: see Fig. 4.

the same solutions and membranes used in the electrowinning experiments were conducted without external potential (i.e., diffusion experiments).

In the diffusion experiments, only ion diffusion should occur, that is, anions exchange between the catholyte and the ampholyte and cations exchange between the ampholyte and anolyte. Figure 10 shows the possible ion transport in the cell, but the diffusion is controlled by the charge neutrality in the electrolytes, that is, no net charge transfer across the membranes. The ion transport is dominated by the ion concentration gradients between the three electrolytes.

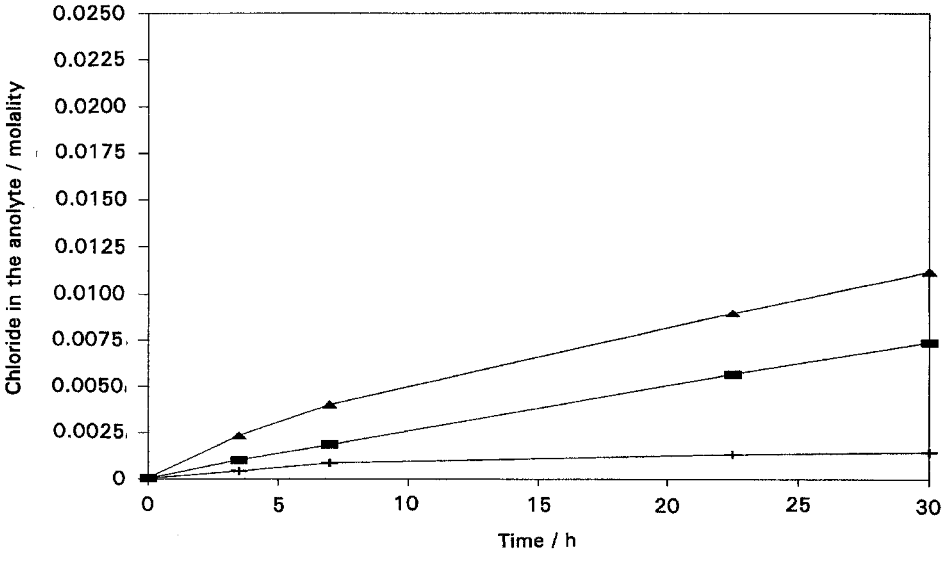

Fig. 9. Chloride concentration in the anolyte as function of time during the electrowinning of nickel chloride. Key: see Fig. 4.

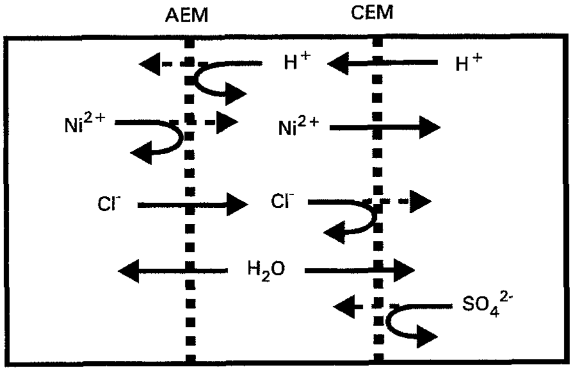

Fig. 10. Simplified diagram. (Nonhydrated ion and water transport in the two membrane cell during the diffusion experiment).

As can be seen from Figs 11 and 12, the cation exchange between the anolyte and the ampholyte results in an increase of the acidity and a decrease of nickel concentration in the ampholyte, but the exchange rate in the three types of cation exchange membrane is in the order: Flemion® > Nafion®-117 > Nafion®-350. The diffusion of the nickel ions to the anolyte can not be depressed by an electric field in the self diffusion experiment. Nevertheless, nickel diffuses to the anolyte, as shown in Table 3. It can be postulated that the loss of protons from, and the flux of nickel into the anolyte enhances the second dissociation of sulphuric acid ($K_2 = 1.2 \times 10^{-2}$). The system in equilibrium will require a mixed nickel sulphate/sulphuric acid anolyte. More than half the amount of nickel in the ampholyte diffused to the anolyte as shown in Fig. 11.

The chloride concentration in the ampholyte increased slightly, as shown in Fig. 13, due to the diffusion of chloride through the anion exchange membrane from the catholyte. It was observed that the nickel concentration decreased slightly and the pH changed from 4.5 to 1.4 in the catholytes, hence the chloride diffusion from the catholyte to the ampholyte is limited by the leakage of nickel ions and protons through the anion exchange membrane due to the requirement of charge neutrality in the catholytes.

The influence of the applied external potential difference over the electrowinning cell on chloride diffusion to the anolyte is puzzling. The results turned out contrary to our expectations. Comparing Fig. 14 with Fig. 9, in the diffusion experiments the chloride concentrations in the anolyte with all three types of

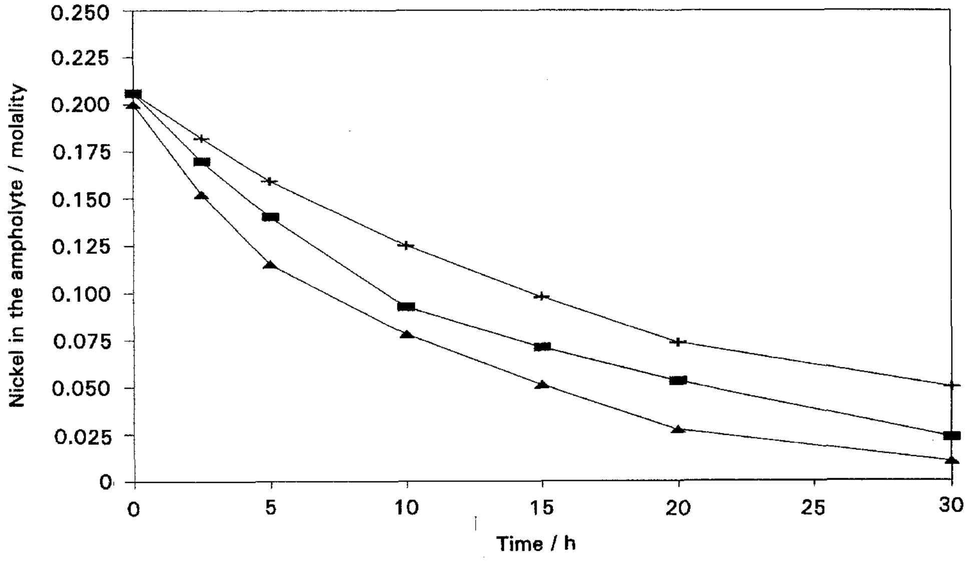

Fig 11. Nickel concentration in the ampholyte as function of time in diffusion experiment. Key: see Fig. 4.

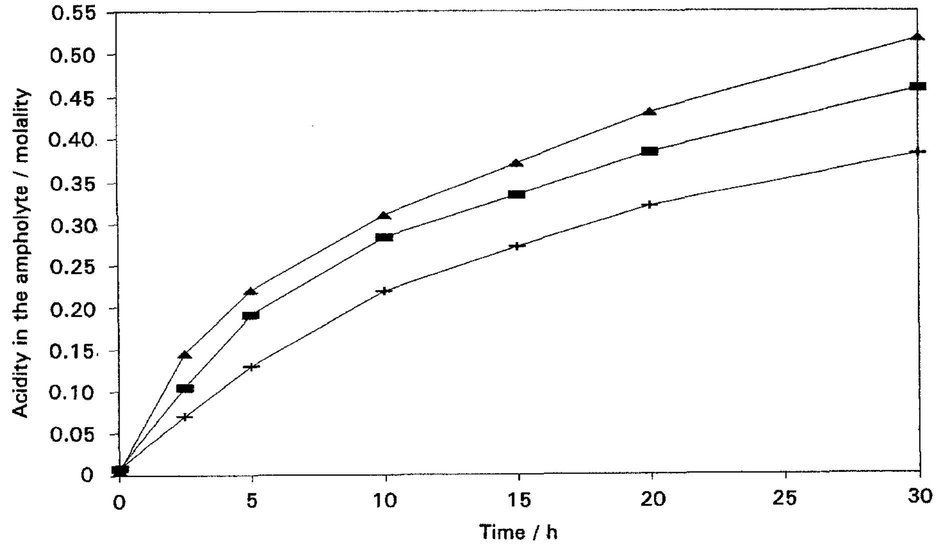

Fig. 12. The acidity of the ampholyte as function of time in the diffusion experiment. Key: see Fig. 4.

Table 3. Nickel and chloride concentration in the anolyte after operating for 30 h

		Nafion®-117	*Nafion®-350*	*Flemion®*
Nickel in the anolyte/molality	self diffusion	0.176	0.147	0.178
	electrowinning	0.114	0.0723	0.131
Chloride in the anolyte/molality	self diffusion	0.0207	0.00376	0.0235
	electrowinning	0.00728	0.00141	0.0113

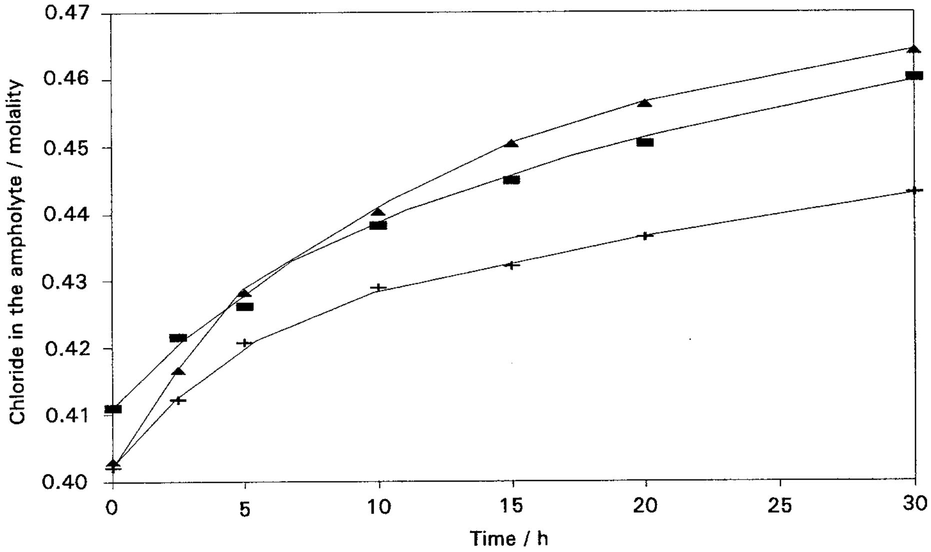

Fig. 13. Chloride concentration in the ampholyte as function of time in the diffusion experiment. Key: see Fig. 4.

cation exchange membrane are higher than that in the electrowinning experiment. The chloride leakage to the anolyte appears to be related to the nickel transport to the anolyte. Table 3 shows the amount of nickel and chloride transported from the ampholyte to the anolyte after 30 h of operation in the two membrane cell with the three types of cation exchange membrane. The more nickel transports from the ampholyte to the anolyte, the more chloride leaks to the anolyte. It would mean that the transport of cations through the cation exchange membrane also creates opportunities for the leakage of anions, probably in the form of ion-couples or complexes, such as $Ni(H_2O)_6Cl^+$ [8,9]. The performance of the three types of cation exchange membrane in preventing leakage of chloride to the anolyte is in the order: Nafion®-350 ≫ Nafion®-117 > Flemion®.

In general, ion transport through the membrane is always accompanied by solvent transport. Because the hydration number for different ions varies, there will be some water transport across the membrane. In the present experiments, no large scale water transport across the membrane was obvious from the lack of change in the liquid level in the three compartments.

4. Conclusions

During the electrowinning of nickel chloride, the ion transport in a two membrane cell can produce a highly

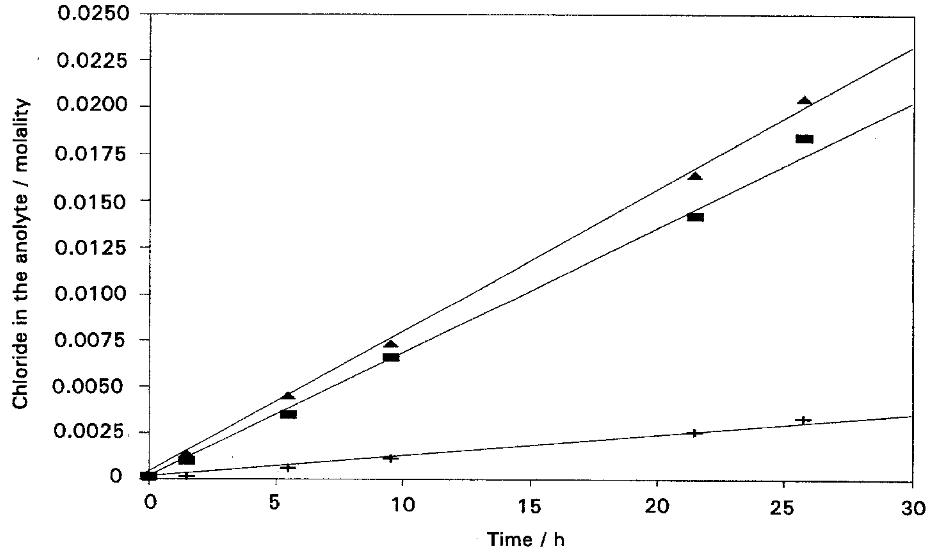

Fig. 14. The chloride concentration in the anolyte as function of time in the diffusion experiment. Key: see Fig. 4.

acidic solution, called the ampholyte. This makes the regeneration of chloride in the form of HCl worthy of further investigation. An acceptable cell voltage (below 3.2 V) and cathodic current efficiency (= 95%) were measured in the two membrane cell. The chloride leakage to the anolyte through the three types of cation exchange membrane increases in the order: Nafion®-350 $\ll$ Nafion®-117 < Flemion®. The external applied potential difference over the cell depresses this chloride leakage rate.

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