THE APPLICATION OF ION EXCHANGE MEMBRANES IN CHLORIDE RELATED ELECTROCHEMICAL TECHNOLOGY

离子交换膜在氯相关的电化学技术中的应用

Proefschrift

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door

Lun-Zhi LIAO

master of science in inorganic chemistry, Yunnan University

geboren te Xingguo, Jiangxi, P.R. China
Dit Proefschrift is goedgekeurd door de promotoren:

Prof. dr. ir. G. Van Weert, M.A.Sc.
Prof. dr. J.H.W. de Wit

Samenstelling promotiecommissie:

Rector Magnificus, voorzitter
Prof. dr. ir. G. Van Weert
Prof. dr. J.H.W. de Wit
Prof. dr. ir. R. Winand
Prof. dr. H. Hurwitz
Dr. A. van Sandwijk
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Lun-Zhi Liao
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Printed in the Netherlands
To my family, especially Yanping and Xinxin
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Chapter 1

GENERAL INTRODUCTION

1. INTRODUCTION

The world demand for metallic materials is still increasing, while the per capita consumption of metals may show a downward trend (i.e. steel), total tonnage does not. This puts pressure on the mining and metallurgical industry, to find new primary resources, but also to develop processes for recycling secondary resources, better known in the industry as “scrap”. New primary resources are often more complex than the one's being replaced. Secondary resources certainly are. Both call for innovative approaches to extractive metallurgy.

Extractive metallurgy as defined by Kirk-Othmer deals with the extraction of metals from naturally occurring compounds and their refinement to a purity suitable for commercial use[1]. The history of extractive metallurgy can be divided into two periods - the ancient period, when only a small number of metals was known, and the recent period, of about the last two centuries, when all other metals have become available commercially.

The types of processes which can be used to produce given metal depend on the characteristics of the ores and the purity requirements to the metals.

Hydrometallurgy is a relatively new discipline compared to pyrometallurgy. Within hydrometallurgy, chloride metallurgy is an even more recent entry compared to sulphate metallurgy. In recent years, research into chemical processes for treating base metal-containing raw materials, including complex sulphide concentrates, is increasingly directed toward chloride hydrometallurgy. Compared to sulphate hydrometallurgy, the main advantages of chloride hydrometallurgy are:
Hydrochloric acid is a very strong lixiviant. Compared to sulphuric acid solution, a much higher proton activity can be achieved in hydrochloric acid solution[2].

In chloride hydrometallurgy hydrogen sulphide or elemental sulphur can be produced instead of problematic sulphates[3].

Chlorides generally are more soluble than sulphates, allowing more concentrated solution to be processed at lower capital costs.

Ease of separation of many metal chlorides through processes such as ion exchange, solvent extraction, valency changes, precipitation and crystallisation.

The ability to manipulate pH and redox in process solutions simultaneously and independently over their entire ranges.

For carrying out hydrometallurgical processes in an economically and environmentally acceptable way, the most important precondition is that methods must be available which permit not only the recovery of metals but also the regeneration of lixiviant, so that it may be recycled for further treatment of raw materials. Preferably, the lixiviant utilised should be regenerated as its original specie, even when hydrochloric acid is used as lixiviant for base metal mineral leaching, in the electrowinning stage chlorine gas instead of hydrochloric acid is produced at the anode. The regeneration of hydrochloric acid is realised by burning this chlorine gas produced at the anode with hydrogen, followed by an absorption step. Meanwhile, it is not economically and technically attractive to convert metal chloride into metal sulphate before electrowinning. Processes aimed at regenerating chloride in the form of hydrochloric acid by pyrohydrolysis have been extensively reviewed and investigated[4]. However, the standard method of producing non-ferrous metals with recovery of the lixiviant is by electrolytic processes. The electrowinning of metal from a chloride solution without evolution of chlorine, one of the missing links in hydrometallurgy[5], remains a very relevant issue.
2. DIRECT HYDROCHLORIC ACID REGENERATION IN METAL CHLORIDE ELECTROWINNING

2.1. Oxygen anode and hydrogen oxidation in aqueous solution

It has been suggested to evolve oxygen instead of chlorine on the anode by using an oxygen evolution anode[5]. According to the half-cell potentials for the following reactions,

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad E^\circ = 1.36 \text{ V} \]
\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad E^\circ = 1.23 \text{ V} \]

it seems possible thermodynamically to evolve \( \text{O}_2 \) instead of \( \text{Cl}_2 \) on the anode during the electrowinning of metal chloride. However, the overpotential of oxygen evolution on a common anode is much higher than that of chlorine. For instance, the overpotential for chlorine evolution is less than 0.2 V at a current density of 1000 A/m\(^2\) at a graphite anode, while the overpotential for oxygen evolution at the same anodic current density is 0.6 V. Therefore, in practice, chlorine is more easily produced than oxygen.

Theoretically, there might be materials which would reduce the activation energy for oxygen evolution and increase the activation energy of chlorine gas evolution. If this type of materials was found or produced, oxygen may be evolved on such a oxygen anode before chlorine and the missing link would be realised. Unfortunately, a thorough study of literature data on the mechanism of oxygen and chlorine evolution on existing materials ended with a disappointing conclusion on the feasibility of such anode materials.

Another possibility exists, namely to regenerate HCl by introducing an extraneous reducing agent into the system. This reducing agent should be oxidised at the anode at lower potentials than chloride. In order to regenerate chloride in the form of HCl, it is essential for the extraneous reducing agent to
provide enough H\(^+\) for the formation of HCl and to compensate the positive charge loss due to the metal deposition on the cathode. When evaluating economical and technological issue, hydrogen and methanol come up as suitable candidates.

Hydrogen is a promising reducing agent due to its low oxidation potential and reasonable price. It is also without environmental problems, although handling in an electrorefinery may have hazards.

\[
H_2 \rightarrow 2H^+ + 2e^- \quad \quad \quad E^0 = 0.00 \text{ V}
\]

When test work was carried out by directly bubbling the hydrogen gas through the anolyte with black platinum as the anode, the anodic current density was found to be determined by the hydrogen concentration on the surface of the anode when the anodic potential was high enough for hydrogen oxidation. The results showed that the maximum hydrogen concentration at the electrode surface was controlled by the relatively low solubility of hydrogen in the aqueous solution. This results in a limiting current density in the order of 10 A/m\(^2\), which is by far not large enough for practical application.

2.2. Electro-oxidation of methanol

Methanol is another promising reducing agent for the regeneration of chloride in the form of HCl, because of its low price and high solubility in aqueous solution. According to:

\[
\text{CH}_3\text{OH} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + 6\text{H}^+ + 6e^- \quad \quad E^0 = 0.044 \text{ V}
\]

methanol can be easily oxidised in quite a low potential range, at least judging from thermodynamics.

The study of electro-oxidation of methanol originated from the idea that the direct methanol-air fuel cell would be an attractive power source for automotive applications. The fuel cell must operate in a acid environment since the
oxidation product, CO₂, will lead to precipitation of carbonates in alkaline electrolytes. This precipitation will result in the plugging of electrode pores, a decrease in the conductivity of the electrolyte, and an increase in concentration polarisation losses[6]. Most investigations on methanol oxidation have therefore been concentrated on acid solution, especially H₂SO₄ and H₃PO₄. The acid environment is unfortunately extremely corrosive to electrode materials, and thus considerably narrows the choice of electrocatalyst material for the oxidation of methanol. During initial stages of fuel cell research, platinum was considered the best anode material for its good resistance to acid and its high catalytic activity over a wide potential range for methanol oxidation.

Therefore methanol oxidation was carried out in a 1.0 M sulphuric acid solution with black platinum as the catalyst also in the present work. A current density in the order of 300 A/m², which is compatible with most base metal electrowinning, was obtained at room temperature. Unfortunately, for a hydrochloric acid solution, the current density fell to 15 A/m², due to the poisoning of the platinum catalyst by chloride.

Separating of the methanol oxidation reaction from the chloride solution would avoid the poisoning of the platinum catalyst. Therefore further research into the application of an ion exchange membrane as a separator device was undertaken.

3. SCOPE OF THIS DISSERTATION

This dissertation has been divided in two parts. The first part deals with the regeneration of hydrochloric acid during metal chloride electrowinning. The tool used to reach this goal is to use ion exchange membranes. Actually, this part includes two different electrode set-ups, i.e. regeneration of hydrochloric acid in a membrane cell with oxygen evolution at the anode, as well as with hydrogen oxidation at the anode. The cell construction for hydrochloric acid regeneration, the behaviour and performance of various types of ion exchange membranes, the cell voltage and electrode potentials have all been investigated.
The second part of this dissertation appears not to have a direct connection with the first part, the production of metals. The second part involves the production of chlorine by hydrogen chloride electrolysis, which seems superfluous to this work's objective. Excess HCl is a problem, however, not only in organic chlorination processes, but also in the minerals processing industry. In particular, the processing of titaniferrous ores requires dry chlorination to yield TiO₂ pigments and chlorine. The iron content of the ore, however, yields FeCl₂ or FeCl₃ and technology to react these compounds with oxygen is not available. As reported before[4], ferrous chloride can be pyrohydrolyzed to Fe₂O₃ and hydrochloric acid. A process to electro-oxidize wet HCl compatible with pyrohydrolysis of iron chloride would meet a technological and economic need. In the second part, the possibility to electrolyse hydrogen chloride to chlorine at a low cell voltage has been investigated.

4. OUTLINE OF THIS DISSERTATION

In Chapter 2, the basic characteristics of ion exchange membranes and their usage are reviewed.

Chapter 3 presents initial experimental results of a membrane cell used in hydrochloric acid regeneration during metal chloride electrowinning[7].

In Chapter 4 the ion transport in the membrane electrowinning cell with and without voltage difference over the ion exchange membrane is described. The performance of various types of cation exchange membranes, with regard to chloride rejection is evaluated and discussed[8].

To further eliminate traces of chlorine gas evolution at the anode, various approaches have been used to reduce chloride leakage to the anolyte, consisting of sulphate solution. The results are presented in Chapter 5[9].

In Chapter 6, results on the regeneration of hydrochloric acid by means of a hydrogen diffusion anode are presented and discussed[10].
The mechanism and electrocatalyst for chlorine evolution are reviewed in Chapter 7.

Chapter 8 gives the electrode potential, especially cathode potential as a function of current density, electrolyte composition and operational conditions during the electro-oxidation of hydrochloric acid for chlorine production[11].

Chapter 9 describes the electrolysis of hydrochloric acid and the reoxidation of low valence metal ions[12].

4. REFERENCES:


Chapter 2

THE THEORETICAL ASPECT OF ION EXCHANGE MEMBRANES

1. INTRODUCTION

Ion exchange membranes became available commercially about forty years ago. These early membranes were sulphonated and aminated derivatives of, usually, phenol-formaldehyde polycondensates. During the 1950's and 1960's the main use that was envisaged for ion exchange membranes was the desalination of brackish water and sea water. These membranes were required to be low cost and strong and to be able to transport large amounts of alkali and alkaline earth ions or halide and other simple inorganic anions. High selectivity and low electro-osmotic transfer in contact with very dilute solutions were needed to give a high current efficiency. The ability to discriminate between counter ions was mainly undesirable because it led to poisoning by heavy metal ions and fouling by organic anions. Low electrical resistance was desirable but not of the highest priority because the resistance of a desalination cell was controlled mainly by that of the dilute stream.

Nowadays, ion exchange membranes have been extensively used as separator in electrochemical systems both with aqueous and non-aqueous electrolytes[1,2,3], such as chlor-alkali cells[4], water electrolyzers[5,6], hydrogen-halogen cells[7,8,9,10,11], zinc-bromine batteries[12].

The application of membrane technology to chlor-alkali industry is possibly one of the greatest contribution of ion exchange membranes. The membrane process was introduced to chlor-alkali industry in 1975. During 1980s membrane technology for chlor-alkali production was established as the optimum commercial technology for new plant installation. Nowadays almost every new plant is built as a membrane plant and about 20% of world chlorine production is produced via the membrane process. Nafion® membranes have contributed significantly to this technological revolution, having been used in the
production of more than 20,000,000 T of caustic in more than 110 chlor-alkali plants[13]. With ion-exchange membrane electrolysis, operation can be realized at a current density more than 3 kA/m². The power consumption for caustic production is expected below 2000 kWh/mt, 35% of energy saving compared to the traditional process. The concentration of sodium hydroxide can reach to 40% directly without significant loss of current efficiency (95%)[14] and the NaOH product contains less than 50 ppm NaCl, while chlorine contains less than 0.5% oxygen.

In this chapter, the characteristics of ion exchange membranes will be reviewed and discussed.

2. A SIMPLIFIED PHYSICAL PICTURE OF ION EXCHANGE MEMBRANE

Ion exchange membranes used present day in electrochemical processes usually are made from ion exchange polymers. Polymeric ion-exchange membranes are membranes made from polymers carrying covalently fixed ionic groups, where either the cation or anion is chemically bound to the polymeric backbone. In contact with a polar liquid like water, the respective counter ion can dissociate and therefore can be exchanged by another ion having the same charge prefix. The dissociation of the counterion leads to selectivity of the ion exchange membrane for counterions. The functional groups dissociate into the counterions of opposite charge which are freely movable in the swollen polymer matrix as shown in Figure 1.

![Schematic of cation exchange polymer](image-url)
The strong Coulomb forces ensure that the charge of fixed ions is always compensated by an equivalent amount of counterions with opposite charge. Different counterions may exchange with each other. For instance, when the cation exchange membrane shown in Figure 1 is placed into a strong acid solution, most of its counterions will be replaced by hydronium ions from the acid. After the membrane is taken out the acid solution, and then washed with deionized water, it still contains the hydronium ions which are kept in the polymer through Coulomb force interaction with the fixed ions. In one aspect the ion exchange membrane may be considered a solid acid. When it is immersed into a NaOH solution, Na\(^+\) from the solution will exchange with hydronium from the "solid acid". The membrane will be neutralized and convert to sodium form.

Ion exchange groups which can be used in cation-exchange polymers are divided into cation exchange group and anion exchange group:

For a cation exchange polymer, exchange groups are divided into three types according to their acidity:

1.) Strong acidic cation-exchange group--Sulfonate group:
   polymers-SO\(_3\)\(^-\) M\(^+\)  \(\text{M}^+ = \text{H}^+, \text{Na}^+, \text{K}^+\)... 

2.) Medium acidic group--phosphonate group:
   polymer-PO\(_3\)\(^2-\) (M\(^+\) \(\text{M}^+ + \text{M}^2+ = \text{Ca}^{2+}, \text{Mg}^{2+} \) ..... 

3.) Weak acidic cation exchange groups--carboxylic group:
   Polymer-CO\(_2\)\(^-\) M\(^+\)  \(\text{M}^+ = \text{H}^+, \text{Na}^+, \text{K}^+\)... 

Nafion® is the earliest representative of the (perfluoro-)sulfonate group cation exchange membranes, which has been widely used in various electrochemical processes. Flemion is the representative of carboxylic group membranes, which also plays an important role in membrane processes. A fluocarbon copolymer containing both carboxylate and sulfonate acid or salt groups, a cation exchange membrane with excellent anion rejection and high caustic efficiency, has also been commercialized by du Pont.
The most common anion exchange groups are listed as follows:

- Quaternary Ammonium Group: Polymer-NR\textsubscript{3}\textsuperscript{+} An\textsuperscript{-} = Cl\textsuperscript{-}, Br\textsuperscript{-} ...
- Quaternary Phosphonium Group: Polymer-PR\textsubscript{3}\textsuperscript{+} An\textsuperscript{-}
- Tertiary Sulfonium Group: Polymer-SR\textsubscript{2}\textsuperscript{+} An\textsuperscript{-}

where R = Alkyl or Aryl group, e.g. C\textsubscript{2}H\textsubscript{5}, C\textsubscript{4}H\textsubscript{9} ....

3. THERMODYNAMIC TREATMENT OF ION EXCHANGE MEMBRANE

A theory of electro-chemical membrane phenomena had been developed by biologists and refined by chemists before ion exchange membranes were available. These theories, known usually as the Teorell-Meyer and Sievers fixed-charge theory[15,16,17,18,19,20] were devoted to the interpretation of potentials and conductance of biological and synthetic membranes with low fixed charge densities and low permeabilities. It followed the lines of the solution-diffusion model but replaced Henry's law by the Donnan distribution to describe the interfacial ionic equilibria and Fick's law by the Nernst-Planck equation to describe ion transport in the membrane.

3.1. Donnan potential and co-ion exclusion

When a cation exchange membrane charged with H\textsubscript{3}O\textsuperscript{+} is placed into pure water, the pH of the water stays almost neutral. The few hydronium ions which diffuse into the water result into a potential difference between the solid electrolyte and the liquid, the so called Donnan-potential. After such diffusion, the ion exchange membrane becomes negatively charged with respect to the liquid which prevents any further diffusion of cations into the liquid. Meanwhile, the negative charge, i.e. the Donnan-potential cation existing in the exchange membrane would also exclude any anions entering the cation exchange polymer. A membrane, made up of cation exchange polymer will therefore act as a barrier for anions as an anion exchange polymer will for cations.
The thermodynamic treatment for the cation exchange membrane used as a separator for two solutions can give a quantitative indication of Donnan-potential. In equilibrium, the i component is freely mobile between one solution phase (s) and the membrane (m), and the following equation is attained:

\[ \mu_i^s = \mu_i^m \]  

(1)

For a simplest 1:1 type of salt, where Z_+ and Z_- are equal to +1 and -1, the chemical potential of the cation and anion in solution and membrane can be written as follows:

For the solution phase,

\[ \mu_+ = \mu_+^o + RT \ln a_+ + F\Psi \]  
\[ \mu_- = \mu_-^o + RT \ln a_- - F\Psi \]  

(2)
(3)

and for the membrane phase,

\[ \bar{\mu}_+ = \bar{\mu}_+^o + RT \ln \bar{a}_+ + F\bar{\Psi} \]  
\[ \bar{\mu}_- = \bar{\mu}_-^o + RT \ln \bar{a}_- - F\bar{\Psi} \]  

(4)
(5)

whenever eliminating electrostatic terms by using equation (1), the following equations are obtained:

\[ RT \ln (\bar{a}_+ \times \bar{a}_-) = RT \ln (a_+ \times a_-) - [ (\bar{\mu}_+^o - \mu_+^o) + (\bar{\mu}_-^o - \mu_-^o) ] \]  

(6)

\[ \bar{C}_+ \bar{C}_- = C_+ C_- \frac{\gamma_+^2}{\gamma_i^2} \exp \left( \frac{-\Delta \mu_i^o}{RT} \right) \]  

(7)

where \[ \mu_i^o = \mu_i^o + \mu_i^o, \quad \bar{\mu}_i^o = \bar{\mu}_i^o + \bar{\mu}_i^o \]

\[ \Delta \mu_i^o = \bar{\mu}_i^o - \mu_i^o, \quad \gamma_+ \gamma_- = \gamma_i^2, \quad \bar{\gamma}_+ \bar{\gamma}_- = \bar{\gamma}_i^2 \]  

(8)
Since electroneutrality is attained in the solution and membrane phase,

\[ C_s = C_r = C \quad \text{ (salt concentration)} \quad (9) \]

\[ \bar{C}_s = \bar{C}_r + \Phi X \]

where \( X \) is the fixed charge (negative) density in the membrane phase. Since the activity is different between a counterion in the neighborhood of a fixed charge and a counter ion entering from the solution phase, one can correct it by \( \Phi \). \( \Phi X \) is therefore called the effective fixed charge density. Substituting Eq. (9) in Eq. (7) yields

\[ (\bar{C}_s + \Phi X)\bar{C}_s = C^2 \frac{\gamma^2}{\gamma_z} \exp\left(\frac{-\Delta \mu^o_z}{RT}\right) = C^2 K_z^2 \quad (10) \]

where \( K_z^2 = \frac{\gamma^2}{\gamma_z} \exp\left(\frac{-\Delta \mu^o_z}{RT}\right) \quad (11) \)

Solving Eq. (10) for \( \bar{C}_s \) gives:

\[ \bar{C}_s = \frac{-\Phi X + \sqrt{(\Phi X)^2 + (2K_zC)^2}}{2} \quad (12) \]

Using Eq. (9) yields

\[ \bar{C}_s = \frac{\Phi X + \sqrt{(\Phi X)^2 + (2K_zC)^2}}{2} \quad (13) \]

Equation (12) and (13) are called Donnan Distribution Equations.
Figure 2. Relationship between ion concentration of $\tilde{C}_i$ and $\tilde{C}_-$ in membrane phase and ion concentration in solution phase $C$ without any applied electric potential.

Figure 2 shows that the filter function of ion exchange membranes is only perfectly effective in dilute solution where the ionic concentration in the liquid is lower than in the polymer, so that the Donnan-potential due to a cation concentration gradient can build up. Otherwise pairs of cations and anions could diffuse together into and through an ion exchange polymer. A consideration of electrolyte concentrations should be taken into account in electro-membrane processes.

When component $j$ permeates an ion exchange membrane at pressure $P$ in a liquid system, the chemical potential of $j$ may be written as

$$\mu_j = \mu^o_j + RT \ln a_j + Z_j F \psi + \nu_j \psi P$$  \hspace{1cm} (14)

By using Eqns. (1) and (14), the electrostatic potential difference ($\Delta \psi$) of the membrane phase from the solution phase can be obtained as reference.

$$\Delta \psi = \bar{\psi} - \psi = -\frac{1}{F} \left[ (\bar{\mu}_i - \mu^o_i) + RT \ln \frac{\bar{a}_i}{a_i} \right]$$  \hspace{1cm} (15)
when the size of anion and cation and the affinity to the polymer are approximately the same,

\[ \overline{\mu}_+^a - \mu_+^a \approx \overline{\mu}_-^a - \mu_-^a \approx \frac{1}{2} \Delta \mu_+^a \]

when \( \overline{\gamma}_+ = \overline{\gamma}_- \) and substituting Eq.(13) in Eq. (15), one obtains

\[ \Delta \psi = -\frac{RT}{F} \left( \ln \frac{1}{K_+} + \ln \frac{C_i}{C_i} \right) = -\frac{RT}{F} \left[ \ln \left( \frac{\Phi X}{2K_+C} + \sqrt{\left( \frac{\Phi X}{2K_+C} \right)^2 + 1} \right) \right] \]  \( (16) \)

This is called the equation of Donnan potential. From Figure 2, it can be seen that when the salt concentration is high compared to a fixed-charge density, the Donnan potential \( \Delta \psi \) is very small. When the salt concentration is low, the absolute value of \( \Delta \psi \) increases. When a cation exchange membrane is in contact with a solution, there are negative fixed charge ions and the same amounts of freely mobile counterions in the membrane phase and freely mobile anions and cations in the solution phase. The free ions tend to be homogeneous in both phases because of thermal motion, resulting in the transport of counterions to the solution phase and co-ions to the membrane phase. Therefore, the membrane phase is charged negatively and the solution phase is positive at the interface of membrane and solution.

3.2. The selectivity of (cat)ion exchange membrane

Selectivity is another important parameter for ion exchange membrane used in electrochemical processes. The selectivity of a cation-exchange membrane in aqueous media has been reported in recent examination[21]. The preference of one ion for another in the resin phase is primarily dependent on the difference in interaction of various ion competing with water[21]. In an aqueous mixture of two simple uni-univalent electrolytes, say MX and NX, equilibrated with a cation-exchange resin, the chemical potential, \( \mu \), of every resin-permeable component is equal in the two phases as shown in Eq.(17),
\[ \mu_{MX} = \bar{\mu}_{MX}, \quad \mu_{NX} = \bar{\mu}_{NX} \text{ and } \mu_{H_2O} = \bar{\mu}_{H_2O} \] (17)

where \( \mu \) and \( \bar{\mu} \) are the chemical potential in solution phase and resin phase, respectively.

By assuming that the chemical potentials in an isothermal system can be divided into two additive terms, one depends only on composition and another one only on pressure. The chemical potential of each component \( i \) \((i = MX, \text{NX, } H_2O)\) in a solution under a concentration \( m \) mole and a pressure \( P \) is given by

\[ \mu_i(P, m) = \mu_i(P^o, m) + (P - P^o)V_i \] (18)

where \( P^o \) is the standard pressure and \( V_i \) is the partial molar volume of component \( i \), meanwhile,

\[ \mu_i(P, m) = \mu_i^o(P) + RT \ln a_i, \] (19)

where \( \mu_i^o \) and \( a_i \) is standard chemical potential and activity of component \( i \).

By combining Eqs. (18) and (19), one can obtain

\[ \mu_i(P, m) = \mu_i^o(P^o) + RT \ln a_i + (P - P^o)V_i \] (20)

when \( V_i \) is independent of composition and pressure without causing serious error.

In equilibrium the osmotic pressure \( \pi \) in the resin phase is equal to the \((\bar{P} - P)\) and is related to the water activity in the resin phase and solution phase,

\[ \pi = -\frac{RT}{V_w} \left( \ln \frac{\bar{a}_w}{a_w} \right) \] (21)
With the above analysis, the chemical potentials of MX and NX in each phase can be given by

\[
\mu_{_{\text{MX}}} = \mu_{_{\text{MX}}}^{\circ} + RT \ln a_{_{\text{MX}}} + PV_{_{\text{MX}}} \tag{22}
\]

\[
\overline{\mu}_{_{\text{MX}}} = \overline{\mu}_{_{\text{MX}}}^{\circ} + RT \ln \overline{a}_{_{\text{MX}}} + \overline{P}V_{_{\text{MX}}} \tag{23}
\]

\[
\mu_{_{\text{NX}}} = \mu_{_{\text{NX}}}^{\circ} + RT \ln a_{_{\text{NX}}} + PV_{_{\text{NX}}} \tag{24}
\]

\[
\overline{\mu}_{_{\text{NX}}} = \overline{\mu}_{_{\text{NX}}}^{\circ} + RT \ln \overline{a}_{_{\text{NX}}} + \overline{P}V_{_{\text{NX}}} \tag{25}
\]

For the equilibrium state, ion exchange between the membrane and the solution for MX and NX can be expressed by

\[
\overline{\text{MX}} + \text{NX} \leftrightarrow \text{MX} + \overline{\text{NX}}
\]

\[
RT \ln \left( \frac{a_{_{\text{MX}}}}{a_{_{\text{NX}}}} \right) = \pi (V_{_{\text{MX}}} - V_{_{\text{NX}}}) = \overline{\mu}_{_{\text{MX}}}^{\circ} + \mu_{_{\text{NX}}}^{\circ} - \mu_{_{\text{MX}}}^{\circ} - \overline{\mu}_{_{\text{NX}}}^{\circ} \tag{26}
\]

By choosing the same standard state on the membrane and solution phases for the reacting components, the sum on the right side of Eq.(26) is zero and

\[
RT \ln \left( \frac{a_{_{\text{MX}}}}{a_{_{\text{NX}}}} \right) = \pi (V_{_{\text{MX}}} - V_{_{\text{NX}}}) \tag{27}
\]

In most membrane phases the \(\pi (V_{_{\text{M}}} - V_{_{N}})\) term is sufficiently small to be neglected and (27) becomes:

\[
\ln \frac{a_{_{\text{MX}}}}{a_{_{\text{NX}}}} \approx \ln \frac{\overline{a}_{_{\text{MX}}}}{\overline{a}_{_{\text{NX}}}} \tag{28}
\]
By substituting the product of molality and activity coefficient for the activity of each ionic constituent of the system in above equation,

$$\ln \left( \frac{m_{M^+}}{m_{N^+}} \right) \left( \gamma_{M^+} \right) \left( \gamma_{X^-} \right) \approx \ln \left( \frac{m_{M^+}}{m_{N^+}} \right) \left( \gamma_{M^+} \right) \left( \gamma_{X^-} \right)$$

(29)

$$\ln \left( \frac{m_{M^+}}{m_{N^+}} \right) \left( \gamma_{N^+} \right) \left( \gamma_{X^-} \right) \approx \ln \left( \frac{m_{M^+}}{m_{N^+}} \right) \left( \gamma_{N^+} \right) \left( \gamma_{X^-} \right)$$

(30)

$K_{EX}$ is so called selectivity coefficient, i.e. the molality product ratio at equilibrium.

For multivalent cation-exchange reactions, the selectivity coefficient can be expressed as

$$\ln K_{EX} = \ln \frac{\gamma_{M^+} \gamma_{X^-}^{z_M z_X} \gamma_{X^-}^{z_M z_X}}{\gamma_{N^+} \gamma_{X^-}^{z_N z_X} \gamma_{X^-}^{z_N z_X}}$$

(31)

From the selectivity coefficient, the suitability of an ion exchange membrane for a mixed system is predictable.

3.3. Transport in ion exchange membrane

Transport across a membrane takes place when a driving force, i.e. a chemical potential difference or an electrical potential difference, acts on the individual components in the system. The potential difference arises as a result of differences in either pressure, concentration, temperature or electrical potential. Membrane processes involving an electrical potential difference occur in electrodialysis and other related processes. The nature of these processes differs from that of other processes involving a pressure or concentration difference as the driving force, since only charged molecules or ions are affected by the electrical field.
For non-ionic substance transport through uncharged polymeric membranes, the solution-diffusion model was well established by the time ion exchange membranes became available[22]. According to this theory transport through a membrane separating two reservoirs was a relatively slow process controlled by the rate of the molecular Brownian motion in the membrane itself. It was postulated that existence of non-equilibrium transport processes did not disturb the maintenance of a thermodynamic equilibrium distribution of the transported substance between the membrane material and the ambient liquid phase at the membrane surface. Thus the concentrations in the membrane at its surface could be uniquely related to the concentration or partial pressures in the external phase, assumed to be homogenous and well-stirred, by experimentally determinable partition or solubility coefficients[23].

The movement of ions across an ion exchange membrane corresponds to an electrical current. If $N_i$ denotes the molar flux density $[\text{mol/(m}^2 \text{s})]$ of the ionic species $i$ with charge $z_i$, Faraday's law applies:

$$j = \frac{I}{A} = \sum_{i=1}^{i} N_i z_i = F \sum_{i=1}^{i} z_i N_i$$  \hspace{1cm} (32)

where $j$ is the current density and $A$ the cross-section area of membrane. The transport of ionic species can generally be accomplished by three different mechanisms: convection, diffusion and migration

$$N_i = N_{i}^{\text{Conv}} + N_{i}^{\text{Diff}} + N_{i}^{\text{Mig}}$$  \hspace{1cm} (33)

When only one spatial coordinate $z$ or $x$ is considered, in dilute systems, the overall or convective velocity can be approximated with sufficient accuracy by the velocity $v$ of the solvent, hence

$$N_{i}^{\text{Conv}} = v C_i$$  \hspace{1cm} (34)

This means that the contributions of the ionic fluxes due to diffusion and migration will not be considered in the overall velocity. The diffusion flux of
component I will be considered independent of the diffusive fluxes of other components (dilute solutions), hence,

$$ N_i^{\text{diff}} = -D_i \frac{dc_i}{dx} \quad (35) $$

where $D_i$ is the diffusivity of component $i$ in the solvent.

Since the force $F_i$ upon a charged molecule of charge $z_i$ in an electric field of gradient $\frac{d\phi}{dx}$ is given by

$$ F_i = -z_i e \frac{d\phi}{dx} \quad (36) $$

the molar flux density $N_i^{\text{mig}}$ (the so-called ionic migration) can be described by

$$ N_i^{\text{mig}} = -z_i u_i c_i \frac{d\phi}{dx} \quad (37) $$

where the ionic mobility $u_i$ is a proportional constant, for the mobility of ion $i$ (together with its solvation shell) in a given solvent. $u_i$ can only be considered constant and independent of other ions in a limit of sufficiently dilute systems.

From Eqns. (33) to (37) the well-known Nernst-Planck equation for ionic transport in dilute electrolyte is obtained:

$$ N_i = v c_i - D_i \frac{dc_i}{dx} - u_i z_i c_i \frac{d\phi}{dx} \quad (38) $$

If $N_i$ is known, a material balance for each ionic species $i$ can be formulated.

Electrical potential is a very strong driving force in comparison to pressure, which is very weak. A concentration term of unity equals to an electrical
potential difference of 1/40 V (for \( z_i = 1 \)) whereas a pressure of 1200 bar is needed to produce the same driving force for water transport[24].

4. THE PROPERTIES OF ION EXCHANGE MEMBRANES

4.1. Osmotic pressure and the swelling of ion exchange membrane

When an ion exchange membrane is placed in a solution, due to concentration gradients between the ion exchange polymer and the outside electrolyte solution, osmotic forces on the non-charged molecules of the solvent have also to be taken into account. If the concentration in the outside solution is lower than that in the membrane, the solvent molecules, such as water molecules, tend to diffuse into the polymer to dilute this concentration. This results into a substantial swelling of the polymer. If the polymer is cross-linked, an equilibrium between the osmotic pressure in the pores (the swelling pressure) and the contractile forces of the polymer network (the contractile pressure) is finally reached. The osmotic pressure difference between the inside and the outside of ion exchange membrane can be expressed by van t’Hoff’s law:

\[
\Delta \pi = RT \Delta c
\] (39)

where \( \Delta c \) is the total concentration difference of movable species (ions and molecules) between the inside pore liquid and the solution outside of the ion exchange membrane. The osmotic pressure difference can easily amount to several bar in conventional ion exchange resins. If the polymer is not sufficiently cross-inked, the polymer will be broken by the osmotic pressure.

4.2. The Swelling of ion exchange membrane

When immersed in aqueous solutions ion exchange membranes swell and imbibe water as well as ions. Without this water to dissociate the ions and plasticize the polymer the conductance of membrane in use today would be too low for practical exploitation.
Four factors can be distinguished as driving water into the membrane [25]. Firstly Polymers tend always to absorb solvents to increase their total configuration entropy. The extent to which water is absorbed is determined by the hydrophobic hydrophilic balance of the polymeric material to which the fixed ions are attached. Usually the hydrophobic character predominates and the swelling would not be large but addition polymer networks and polycondensates may differ considerably, the latter being more hydrophilic than the former. Secondly, the fixed charge and counterions will readily bind water of hydration to extents which depend on the size, charge and polarizability of ions concerned. There is no reason why the hydration tendencies of ions in a membrane should differ markedly from their behaviors in simple solutions. Thirdly, once hydrated, the counterions and fixed charges become dissociated and the normally higher molarity in the membrane than in the surrounding solution creates an osmotic pressure driving more water into the membrane. Fourthly, the dissociation of the counterions from the fixed charges exposes them to electrostatic repulsions along the chains which, just as polyelectrolytes, extends them and expands the network still further.

The extent of swelling is limited by the elastic tensions set up in the chain segments running between fixed points. In early membranes the fixed points were chemical crosslinks between the chains but other types of non-swelling inclusions exist in more modern membranes.

Particularly interesting is the way in which the extent of swelling varies with the concentration of ambient solution. Transferring a membrane from pure water to a dilute solution results in a marked shrinkage, greater than can be accounted for by the change in osmotic pressure. It is probable that the introduction of even a small concentration of sorbed electrolyte decreases the repulsions between the fixed charges and permits the polymer chains to adopt a less extended conformation[26].
4.3. Operating conditions of ion exchange membrane

In electrochemical processes, the important operating condition parameters include current density, temperature, electrolyte concentration. In membrane processes these characteristics have to be taken into consideration.

The upper limit of current density is related to membrane capacity. Fortunately most electrochemical processes operate at current densities below the capacity of membrane. Even for high current density process such as chlor-alkali electrolysis, membrane can operate successfully at current densities more than 4 KA/m$^2$. The lower limit on current density is not set to protect the membrane. Even at very low current densities the membrane functions normally, but diffusion plays a relatively more important role. In the chlor-alkali process, the current efficiency can decline at a lower current density, and caustic purity may be affected by increased chloride and chlorate diffusion.

The membrane is an electrolyte solution, and like electrolytes generally, increases in conductivity with rising temperature. The rate of ion transport across ion exchange membrane is promoted by temperature. In the chlor-alkali process, the dependence of the migration rate of sodium across cation exchange membrane on temperature is not a question of a few percent variation over 10°C. It is factors of three or more, approaching an order of magnitude[27]. Temperature not only affects the conductivity, it also affects water content in membrane. When temperature is too high, it could result into a high vapor pressure within the membrane to form voids in the polymer.

The capacity of the membrane is proportional to the membrane water content. Water content is quite variable and is determined by the concentrations of the anolyte and the catholyte. The membrane in the electrolytic cell can be regarded as an electrolyte "solution" separating the catholyte and anolyte solutions. The available water will distribute itself among the three electrolytes. The more water available, the greater the membrane capacity. A compromise should be made to reach a acceptable electrolyte concentration and a reasonable membrane capacity.
5. LIST OF SYMBOLS:

\( \mu \)  
chemical potential

\( \mu^o \)  
standard chemical potential

\( \mu_j \)  
chemical potential of \( j \) component in solution phase

\( \mu_i^m \)  
chemical potential of \( j \) component in membrane phase

\( \mu_+ \)  
chemical potential of cation in solution phase

\( \mu_- \)  
chemical potential of anion in solution phase

\( \bar{\mu}_+ \)  
chemical potential of cation in membrane phase

\( \bar{\mu}_- \)  
chemical potential of anion in membrane phase

\( \bar{\mu}_+ \)  
mean chemical potential of anion and cation in solution phase

\( \bar{\mu}_+ \)  
mean chemical potential of anion and cation in membrane phase

\( R \)  
gas constant, \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)

\( T \)  
temperature (K)

\( a_+ \)  
mean activity

\( a_j \)  
activity of \( j \) component (M)

\( a_+ \)  
activity of cation

\( a_- \)  
activity of anion

\( \bar{a}_+ \)  
activity of cation in membrane phase

\( \bar{a}_- \)  
activity of anion in membrane phase

\( C \)  
concentration of

\( C_+ \)  
concentration of cation

\( C_- \)  
concentration of anion

\( \bar{C}_+ \)  
concentration of cation in membrane phase

\( \bar{C}_- \)  
concentration of anion in membrane phase

\( \Delta c \)  
concentration difference

\( F \)  
Faraday constant (96500 A s mol\(^{-1}\))

\( \Psi \)  
electrostatic potential

\( \bar{\Psi} \)  
electrostatic potential in membrane phase

\( \gamma \)  
activity coefficient of

\( \gamma_+ \)  
activity coefficient of cation

\( \gamma_- \)  
activity coefficient of anion

\( \bar{\gamma}_+ \)  
activity coefficient of cation in membrane phase

\( \bar{\gamma}_- \)  
activity coefficient of anion in membrane phase

\( \gamma_s \)  
mean activity coefficient of anion and cation in solution phase

\( \bar{\gamma}_s \)  
mean activity coefficient of anion and cation in membrane phase

\( X \)  
fixed charge density in membrane

\( K_\Lambda \)  
partition coefficient of

\( P \)  
pressure

\( v_j \)  
molar volume of \( j \) component

\( V_i \)  
partial molar volume of \( i \) component

\( \pi \)  
osmotic pressure
The theoretical aspect of ion exchange membrane

\[ \Delta \pi \] osmotic pressure difference
\[ K_{\text{selectivity}} \] selectivity coefficient
\[ A \] surface area of (m\(^2\))
\[ j \] current density
\[ N \] molar flux density of (mol m\(^{-2}\) s\(^{-1}\))
\[ N_i \] molar flux density of \(i\) component (mol m\(^{-2}\) s\(^{-1}\))
\[ N_{i,\text{conv}} \] flux of \(i\) component by convection
\[ N_{i,\text{diff}} \] flux of \(i\) component by diffusion
\[ N_{i,\text{mig}} \] flux of \(i\) component by migration
\[ z_i \] charge number of \(i\) component
\[ D_i \] diffusivity of \(i\) component in solvent
\[ u_i \] ionic mobility of \(i\) component
\[ K_{\text{sp}} \] constant of solubility product

6. REFERENCES:

Chapter 3

THE REGENERATION OF HYDROGEN CHLORIDE IN THE ELECTROWINNING OF METAL CHLORIDES IN MEMBRANE EQUIPPED CELLS

ABSTRACT

A new approach to regenerate chloride in the form of HCl, to avoid the anodic production of chlorine during the electrowinning of metal chlorides, is being investigated. The investigation utilized a membrane cell to electrowin copper and nickel chloride. The chloride was recovered in the form of HCl in the catholyte with a single membrane cell and in the membrane compartment solution (ampholyte) with a two-membrane cell. The performance of Nafion-350 to chloride diffusion has been tested in various conditions with a single membrane cell and a two-membrane cell. The performance of Neossepta ACM exchange membrane was also tested.

1. INTRODUCTION

At present, most metal electrowinning occurs in aqueous sulphate solution because of the stability and the low vapour pressure of sulphuric acid. However, it is widely accepted that hydrochloric acid has a greater solubilizing ability than sulphuric acid for certain type of minerals, especially sulphides. When hydrochloric acid is adopted as a lixiviant, the pregnant solution for the electrowinning will be a metal chloride solution. The recovery of chloride from metal chloride electrowinning processes is currently realized in the form of chlorine. The production of chlorine requires a complex, but reliable collection system. It complicates the tankhouse design. In addition, the conversion of chlorine into hydrochloric acid for the leaching stage increases the expenses and complexity of the process, hence the regeneration of chloride in the form of HCl should be given a serious consideration [1].
In previously work, the regeneration of hydrogen chloride by the oxidation of a reducing agent in the anolyte has been investigated. Methanol, one of the promising reducing agents, can be oxidized at a lower electrochemical potential than chloride on the anode, but the best anode material for such oxidation, namely platinum, is rapidly poisoned by the presence of chloride in the anolyte. In order to separate methanol oxidation on a platinum type anode from the chloride solution, the use of a membrane which can prevent chloride diffusion to the anolyte is suggested. In this paper, the possibility of the application of Nafion 350 and Neosepta ACM membranes for chloride regeneration in the form of HCl during the electrowinning of metal chloride is studied. This allows the use of an Pb/Sb anode, with H₂SO₄ solution as the anolyte. Methanol oxidation in this system, if successful, will be reported at a later date.

2. EXPERIMENTAL

The single ion exchange membrane cell used in this work is composed of an anodic compartment and a cathodic compartment separated by a Nafion-350 exchange membrane. The two membrane cell is composed of three

![Figure 1. The Schematic Cross Section of the Membrane Cell.](image-url)
compartments, i.e. anodic, cathodic and membrane compartment. Nafion-350 exchange membrane is used for separating the anodic compartment from membrane compartment; a Neosepta ACM membrane is used for separating the cathodic and membrane compartment. The two-membrane cell, constructed from 10 mm perspex, is shown schematically in Figure 1. The single membrane cell is constructed from the same material with only a Nafion-350 membrane installed in the middle.

Nafion-350 exchange membrane is a cation exchange membrane from Du Pont Company and the Neosepta ACM membrane is an anion exchange membrane from Tokuyama Soda. The diffusion rate of chloride through the Nafion-350 membrane was measured without and with an applied potential difference over the membrane; the latter were conducted during the electrowinning experiment. In the electrowinning experiment, a potentiostat with the software CMS100 from 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 and a lead-antimony plate was used as the anode. The cathode and catholyte were varied depending on the purpose of the experiment. The dimensions of all cell compartments were $100 \times 100 \times 150$ mm.

All the chemicals were of chemically pure grade.

3. RESULTS AND DISCUSSION

3.1. Chloride diffusion in the one-membrane cell without electrode potential

The measurement of the chloride diffusion rate without applied potential difference over the membrane was conducted in the single membrane cell. The anolyte was 2.0 M $\text{H}_2\text{SO}_4$ solution and the catholyte was a 3.0 M hydrochloric acid solution. The chloride concentration in $\text{H}_2\text{SO}_4$ solution measured as a function of time is shown in Figure 2. Although it was suggested by the supplier that Nafion-350 membrane has a good selectivity for cations, especially for preventing chloride permeation, it can be seen from Figure 2 that a large amount of chloride can go
through the Nafion-350 membrane under the test conditions. A little bit higher chloride concentration was obtained in the H₂SO₄ solution when the cathodic side of membrane faced the H₂SO₄ solution.

Not only was chloride found in the sulphuric acid solution, but a certain amount of sulphate ions was also detected in the hydrochloric acid solution. After twelve hours, a liquid level difference was observed in the cell, probably caused by osmotic pressure. Because cations and anions, even H₂O, can go through Nafion-350 exchange membrane, it seems that the Nafion-350 exchange membrane has no selectivity under the test conditions. When 1.5 M NaCl solution is put in the cathodic side of Nafion-350 membrane and pure water is put in the other compartment of the single membrane cell, after sixteen hours, no chloride was detected in the water. It means that the chloride diffusion through Nafion-350 membrane depends on the electrolyte composition. Further investigation is needed to understand Cl⁻ migration through Nafion membrane.

![Graph](image)

Figure 2. Chloride diffusion as a function of time at room temperature.
3.2. Chloride diffusion in the one-membrane cell during the electrowinning experiment

The initial experiments were carried out with a lead-antimony sheet as the anode and a sulphuric acid solution as the anolyte to test the performance of Nafion-350 to chloride diffusion under conditions of the electrowinning. Then, protons are produced by the oxidation of H₂O and oxygen is evolved on the anode. If a low level of chloride concentration is maintained in the anolyte by the membrane separation, no attack of the lead/antimony anode will occur. The chloride diffusion rate was measured during copper and nickel electrowinning experiments.

In copper the electrowinning experiment, the catholyte was a 0.7 M CuCl₂-2.0 M NaCl-2.0 M HCl solution. A piece of stainless steel was used as the cathode. A 2.0 M H₂SO₄ solution was used as the anolyte and a 30 cm² Pb-Sb sheet as the anode. The catholyte was covered by a layer of 2 cm thickness of paraffin to prevent oxidation of Cu⁺ by air. The cathodic current efficiency in this experiment was 95% and the cell voltage 2.4 V at a constant current density of 200 A/m². The anodic potential was about 2.0 V and the cathodic potential about 0.05 V. It means that the total voltage drop due to the resistance of electrolyte and membrane is around 0.4 V. The deposit of copper on the cathode occurred as a compact layer. Unfortunately, the chloride concentration in the anolyte increased to 0.1 M after 6 hours due to diffusion of the chloride from the catholyte.

The experimental conditions and part of the results for the electrowinning of nickel chloride are shown in Table 1.

From Figure 3, it can be seen that the pH of the catholyte was decreasing as the electrowinning proceeded, resulting from the transfer of protons from the anolyte. The proton transportation is partly caused by the excess of protons in the anolyte from the oxidation of H₂O and partly by the high acidity of the anolyte. The surplus of chloride ions left by the deposition of nickel will combine with protons from the anolyte to form HCl, so HCl is formed in the catholyte.
Because Nafion-350 is a cation exchange membrane, chloride ions are not expected to permeate the membrane into the anolyte. The chloride diffusion rate from the catholyte into the anolyte was much lower in both nickel electrowinning.

Table 1. Electrowinning Data of Nickel Chloride

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Ni-1</th>
<th>Ni-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catholyte composition</td>
<td>1.0 M NiCl₂</td>
<td>1.0 M NiCl₂</td>
</tr>
<tr>
<td>Anolyte composition</td>
<td>2.0 M H₂SO₄</td>
<td>1.0 M H₂SO₄, 0.5 M Na₂SO₄</td>
</tr>
<tr>
<td>Cathode</td>
<td>pure Ni</td>
<td>pure Ni</td>
</tr>
<tr>
<td>Initial pH in catholyte</td>
<td>1.72</td>
<td>1.89</td>
</tr>
<tr>
<td>Current Density (A/m²)</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Average Cell Voltage(V)</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Cathode Current Efficiency (%)</td>
<td>44 (at 20°C)</td>
<td>56 (at 20°C)</td>
</tr>
</tbody>
</table>

Figure 3. The pH of the catholyte during nickel electrowinning with the Single Membrane Cell. See text for conditions.
experiments as shown in Figure 4, than in the earlier diffusion and copper electrowinning experiments. Chloride concentration in the anolyte was lower than $4 \times 10^{-3}$ M after 20 hours batch-wise experimentation. No chlorine odour was detected over the anodic compartment during the nickel electrowinning process. Only a small amount of chloride permeates through the membrane under these test conditions.

The current efficiency as shown in Table 1 in both experiments is not of the level reported in the literature. It has been reported that the cathode current efficiency is more than 90% when the pH of the catholyte is in the range of 1.0-2.0[2], even 97-98% [3]. A large amounts of hydrogen bubbles were observed in the experiment at room temperature. The low current efficiency is probably resulting from the rapid decrease of the pH in the catholyte. From Figure 3, it can be seen that most of the time electrowinning was conducted at a pH lower than 1.0. The pH of the catholyte in Ni-2 is higher than that in Ni-1, because of the adoption of 1.0 M H$_2$SO$_4$-Na$_2$SO$_4$ as the anolyte in Ni-2 instead of 2.0 M H$_2$SO$_4$ in Ni-1. The higher acidity in the anolyte of Ni-1 resulted in more protons permeating the membrane to the catholyte of Ni-1. Another important reason for the low current density in our experiment is the low temperature (20°C) of the electrolyte instead of 55-60°C as usual. When the temperature of the electrolyte is maintained at 50°C, the current efficiency in Ni-2 is around 80%.

From Figure 4, it also can be seen that certain amount of Ni$^{2+}$ ions can go through the Nafion-350 membrane to the anolyte because of the permeability of Nafion-350 membrane for cations. The transfer of nickel ions to the anolyte may reach an equilibrium level.

3.3. Chloride diffusion in the two-membrane cell during the electrowinning of nickel chloride

To solve the low cathode current efficiency resulting from the high acidity in the catholyte and the loss of nickel due to permeation of nickel to the anolyte, a Two
Figure 4. [Cl] and [Ni$^{2+}$] in the anolyte during nickel electrowinning with Single Membrane Cell.

Figure 5. The [Cl] in the ampholyte and the anolyte during nickel electrowinning with Two Membrane Cell at 20°C.
Membrane (one is cation exchange membrane Nafion-350, another is anion exchange membrane Neosepta ACM) Cell was adopted in the electrowinning experiment. It is expected that the anion exchange membrane can prevent the transfer of protons from the ampholyte to maintain a suitable acidity in the catholyte and the diffusion of nickel ions from the catholyte to the ampholyte. In this way chlorine is regenerated in the form of HCl in the ampholyte. Figure 5 shows that the Neosepta ACM membrane is chloride permeable and a large amount of chloride transferred to the ampholyte, but only a very small amount of chloride diffused to the anolyte during the test period, due to the presence of the Nafion-350 membrane between the ampholyte and the anolyte. This makes the production of HCl possible. Figure 6 shows that the Neosepta ACM membrane displays a good performance in preventing the permeation of Ni$^{2+}$. A very low nickel concentration was detected in the ampholyte when a 0.5 M H$_2$SO$_4$ solution was used as the ampholyte. The Neosepta ACM membrane also displays a good performance in preventing the diffusion of protons as shown in Figure 6. When the electrowinning experiment was carried out at 20°C, the pH of the catholyte was dramatically increased to more than six after the experiment started one hour, due to the evolution of hydrogen on the cathode when the electrowinning of nickel chloride was carried out the room temperature. The cathode potential became

![Figure 6](image_url). The pH of the catholyte and [Ni$^{2+}$] in the ampholyte at 20°C.
negative to -1.3 V vs S.H.E. at a constant current density of 200 A/m². Only a small amount of nickel was deposited on the cathode and a great number of hydrogen bubbles were evolved on the cathode. Meanwhile, some Ni(OH)₂ precipitation was observed in the cathodic compartment and on the surface of cathode.

Fortunately, when the electrowinning experiment was repeated out at 50°C, the pH of the catholyte was easily maintained around 2.0 and the cathode current efficiency was more than 95%. The cathode potential was only around -0.6 V vs S.H.E., so the production of hydrogen chloride with the Two Membrane Cell in conjunction with nickel chloride electrowinning is promising.

It can be seen from Figure 5 and Figure 6 that the chloride concentrations in the anolyte are around 10⁻³ M. They are much lower than those in the sulphuric acid solution in the diffusion experiment, but it has been reported that 10⁻⁵ M chloride can already reduce the activity of platinum electrode for the oxidation of methanol by a factor of three[4], so the chloride concentration in the anolyte may still be high enough to poison a platinum anode used for methanol oxidation. However, the regeneration of chloride in the form of HCl in the electrowinning of nickel chloride appears possible by the application of lead-antimony anodes in Two Membrane Electrowinning Cells.

4. CONCLUSIONS

1) The permeability of Nafion-350 to chloride is related to the electrolyte solution composition.

2) The regeneration of chloride in the form of HCl in the electrowinning of nickel chloride occurs in the catholyte with a single membrane cell, and in the ampholyte with a two membrane cell. A low chloride concentration in the anolyte appears possible with the two membrane cell.
5. REFERENCES


Chapter 4

ION TRANSPORT IN A TWO MEMBRANE ELECTROWINNING CELL FOR THE PRODUCTION OF HYDROCHLORIC ACID

ABSTRACT:

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 lixivants 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 by-product 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 Figure 1.

![Figure 1](image_url)

**Figure 1.** One process variant by which the two membrane cell could be utilized.
2. EXPERIMENTAL DETAILS

In this work, the composition changes of the anolyte, the ampholyte\(^1\) 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 Figure 2. The compartment between the anode compartment and cathode compartment is named the ampholyte compartment after the electrolyte. The solution content of each compartment was 1000 ml and the effective dimensions of the membrane was 10 \(\times\) 10 cm\(^2\). Three different types of cation exchange membrane listed in Table I 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

\(^1\)The name "ampholyte" is being suggested to denote the electrolyte of the middle compartment. Amphi = (from) both sides.
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

![Diagram of a two-membrane electrowinning cell](image)

Figure 2. Schematic cross section of the Two-Membrane Electrolytic Cell.

Table 1. Characteristics of the membranes investigated.

<table>
<thead>
<tr>
<th>Name</th>
<th>Nafion-117</th>
<th>Nafion-350</th>
<th>Flemion</th>
<th>Neosepta-ACM</th>
</tr>
</thead>
<tbody>
<tr>
<td>type</td>
<td>H⁺</td>
<td>H⁺</td>
<td>H⁺</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>electric resistance/Ohm-cm²</td>
<td>1.5</td>
<td>4.8</td>
<td>1.4</td>
<td>4.0-5.0</td>
</tr>
<tr>
<td>exchange capacity/mequiv g⁻¹</td>
<td>1.1</td>
<td>1.5</td>
<td>1.1</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>thickness/mm</td>
<td>140</td>
<td>250</td>
<td>100</td>
<td>110-130</td>
</tr>
<tr>
<td>reinforcing</td>
<td>No</td>
<td>Yes</td>
<td>no</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Electric resistance: Equilibrated with 0.5 N-NaCl solution, at 25°C.
Exchange capacity: meq g⁻¹. Na-form (or Cl-form) dry membrane.
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 cm². The electrowinning experiments were operated at a current density of 200 Am⁻² and 1.0 M NiCl₂ solution was used as the catholyte. Since the ampholyte consists of spent catholyte, 0.2 M NiCl₂ was arbitrarily selected as the initial ampholyte and 1.0 M H₂SO₄ 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.

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 de-ionized 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 volts at a current density of 183 A m⁻²[6]. A smooth and compact nickel deposit was obtained on the cathode in all experiments.

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

<table>
<thead>
<tr>
<th>Type of membrane</th>
<th>Nafion-117</th>
<th>Nafion-350</th>
<th>Flemion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density/A m⁻²</td>
<td></td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Electrolyte temperature/°C</td>
<td></td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Cathodic potential/V</td>
<td></td>
<td>-0.71</td>
<td></td>
</tr>
<tr>
<td>Anodic potential with Pb-Sb</td>
<td></td>
<td>1.85 V</td>
<td></td>
</tr>
<tr>
<td>Anodic potential with DSA</td>
<td></td>
<td>1.35 V</td>
<td></td>
</tr>
<tr>
<td>Cell voltage with Pb-Sb anode</td>
<td>3.15 V</td>
<td>3.10 V</td>
<td>3.15 V</td>
</tr>
<tr>
<td>Cell voltage with DSA</td>
<td>2.71 V</td>
<td>2.65 V</td>
<td>2.75 V</td>
</tr>
<tr>
<td>Voltage drop over membranes &amp; electrolytes</td>
<td>0.65 V</td>
<td>0.60 V</td>
<td>0.65 V</td>
</tr>
<tr>
<td>Cathodic current efficiency/%</td>
<td>96</td>
<td>97</td>
<td>96</td>
</tr>
</tbody>
</table>
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 Figure 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 transport through the membranes can be deduced from the change of ion concentrations in three electrolytes.

![Figure 3](image-url)  
*Figure 3.* Simplified diagram (Nonhydrated ion and water transport in the two-membrane cell during the electrowinning of nickel chloride).
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 Figure 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 Figure 5, in the same three electrowinning experiments as shown in Figure 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 Figure 6.

From Figure 4 and Figure 6, it can be seen that both the acidity and the chloride concentration in the ampholyte increased with time. Hydrochloric acid is formed.
Figure 4. Nickel concentration of the ampholyte as a function of time when electrowinning nickel chloride.

Figure 5. The acidity of the ampholyte as a function of time when electrowinning nickel chloride.
Figure 6. Chloride concentration in the ampholyte as a function of time in the electrowinning of nickel chloride.

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 Figure 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 Figure 8, is in stoichiometric agreement with the nickel deposition shown in Figure 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 Figure 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 is being designed for improved anion rejection[7].

Figure 7. Nickel concentration in the catholyte as a function of time when electrowinning nickel chloride.
Figure 8. Chloride concentration in the catholyte as a function of time when electrowinning nickel chloride.

Figure 9. Chloride concentration in the anolyte as a function of time during the electrowinning of nickel chloride.
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 the same solutions and membranes used in the electrowinning experiments were conducted without external potential, i.e. diffusion experiments.

![Diagram of ion transport in the two membrane cell](image)

Figure 10. Simplified, i.e. nonhydrated ion and water transport in the two membrane cell during the diffusion experiment.

In the diffusion experiments, only ion diffusion should occur, i.e. 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, i.e. no net charge transfer across the membranes. The ion
transport is dominated by the ion concentration gradients between the three
electrolytes. As can be seen from Figure 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 nickel in the ampholyte diffused to the
anolyte as shown in Figure 11.

![Graph showing nickel concentration in the ampholyte as a function of time in diffusion experiment.]

Figure 11. Nickel concentration in the ampholyte as a function of time in diffusion experiment.
Figure 12. The acidity of the ampholyte as a function of time in the diffusion experiment.

The chloride concentration in the ampholyte increased slightly, as shown in Figure 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 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. Compared Figure 14 with Figure 9, in the diffusion experiments the chloride concentrations in the anolyte with all three types of 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
hour's 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(H₂O)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.

![Graph](image)

Figure 13. Chloride concentration in the ampholyte as a function of time in the diffusion experiment.
Figure 14. The chloride concentration in the anolyte as a function of time in the diffusion experiment.

Table 3. Nickel and chloride concentration in the anolyte after 30 hour operation

<table>
<thead>
<tr>
<th></th>
<th>Nafion-117</th>
<th>Nafion-350</th>
<th>Flemion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel in the</td>
<td>self diffusion</td>
<td>0.176</td>
<td>0.147</td>
</tr>
<tr>
<td>anolyte/molality</td>
<td>electrowinning</td>
<td>0.114</td>
<td>0.0723</td>
</tr>
<tr>
<td>Chloride in the</td>
<td>self diffusion</td>
<td>0.0207</td>
<td>0.00376</td>
</tr>
<tr>
<td>anolyte/molality</td>
<td>electrowinning</td>
<td>0.00728</td>
<td>0.00141</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

During the electrowinning of nickel chloride, the ion transport in a two membrane cell can produce a highly 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 << Nafion-117 < Flemion. The external applied potential difference over the cell depresses this chloride leakage rate.

5. REFERENCES:

Chapter 5

THE REGENERATION OF HYDROCHLORIC ACID IN A TWO MEMBRANE NICKEL CHLORIDE ELECTROWINNING CELL

ABSTRACT

During electrowinning of nickel chloride, hydrochloric acid was regenerated instead of chlorine in a two membrane cell, by segregating the chloride catholyte with an anion exchange membrane, and the sulphate anolyte with a cation exchange membrane from the middle electrolyte (ampholyte) compartment. Successful operation of such a cell depends on controlling chloride leakage through the cation exchange membrane to the anolyte. Small amounts of chlorine gas could be detected in the oxygen evolved at the anode. In this paper, the chloride leakage as a function of various types of cation exchange membrane and different composition of the anolyte is reported and discussed. Ag+ was added to the anolyte to eliminate chloride leakage to the anode. The cell voltage, electrode potential and voltage drop over the membrane as a function of current density has also been investigated.

1. INTRODUCTION

Usually, the final step in base metal hydrometallurgy is to electrodeposit the metal from a purified pregnant solution. Electrowinning has the advantage that it recovers the lixivants 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 by-product chlorine can be used directly for the leaching of metal bearing sulphides or alloys, however, 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 the conversion of chlorine into hydrochloric acid increases process costs. The direct electrolytic regeneration of chloride in the form of HCl is not available as a technical option and should be given serious consideration[1].

In previous work[2,3], 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 such a membrane is not perfect for anion rejection. Small amounts of chloride still leak through the cation exchange membrane to the anolyte and are oxidized at the anode. The evolution of chlorine gas with oxygen at the anode not only reduces the current efficiency, but also causes an environmental problem. For this reason, successful operation of this approach depends on whether chloride leakage through the cation exchange membrane can be stopped. Although the application of hydrogen diffusion anode can avoid evolution of chlorine at the anode[4], the cost and scale-up for this type of anode is still problematic. In this paper, the chloride leakage as a function of various types of cation exchange membrane and the different composition of the anolyte is reported and discussed. Ag+ was added to the anolyte to eliminate chloride leakage to the anode. The cell voltage, electrode potential and voltage drop over the membrane as a function of current density has also been investigated.

2. EXPERIMENTAL DETAILS

All experiments were carried out in a cell built of Perspex. It consists of three compartments of equal dimensions, clamped together with external tie rods, which are separated by one piece of cation exchange membrane (CEM) and one piece of anion exchange membrane (AEM), schematically shown in Figure 1. The compartment between the anode and cathode compartments is called the ampholyte compartment after the electrolyte. The solution content
of each compartment was 1000 ml and the effective dimensions of the membranes were 10 × 10 cm. Two different types of cation exchange membrane, Nafion-350 from Du Pont and CMS from Tokoyama Soda were used, in combination with Neosepta ACM anion exchange membrane.

Figure 1. Cell arrangement for nickel chloride electrowinning; the middle compartment contains the ampholyte.

The electrowinning experiments were conducted at 50°C. The temperature was maintained by operating the cell in a water bath controlled by Thermomix-1480 (Braun Melsungen AG). In the electrowinning experiment, a potentiostat with CMS100 software (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. A dimensionally stable anode (DSA®, titanium plate coated with iridium-mixed oxides) from Magneto-Chemie B.V., the Netherlands was adopted in the electrowinning experiments. The cathode was a plate of pure nickel. The surface area of the anode and the cathode were both 30 cm². The electrowinning experiments were operated at a current density of 200 A/m² and 1.0 M NiCl₂ solution was used as the catholyte. 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.

The chloride concentration in the anolyte was measured with an ion selective electrode (IS-CL chloride electrode, Unicam). The acidity of the anolyte and the ampholyte was measured by titration with sodium hydroxide.

All chemicals were Merk chemical grade. The solutions were prepared by dissolving the salt or diluting the acid in distilled de-ionized water.

3. RESULTS AND DISCUSSIONS

3.1. Operation results for the two membrane cell

3.1.1. Anode behaviour during the electrowinning

In the electrowinning experiment, a piece of DSA® was adapted as the anode for the oxidation of water in the sulphuric acid media. The anode potential for oxygen evolution at a current density 200 A/m² is around 1.41 V vs S.C.E.. Comparing the anodic potential from DSA® with that of a lead-antimony anode at the same current density[3], there is an advantage of 0.4 to 0.45 volts for DSA®. Figure 2 shows the galvanostatic curve of the DSA® used in 1.0 M H₂SO₄ solution. An experiment of 45 hours duration showed that this type of DSA® is very stable in the test condition. The cyclic polarization curve of DSA® in 1.0 M H₂SO₄ solution is shown in Figure 3. It is surprising that a limiting current density 250 A/m² was obtained at an electrode potential of 1.42 V vs S.C.E. This is not consistent with a limiting current density of 1000 A/m² in aqueous solution reported by the producer[5]. However, the testing conditions were different. The coverage of the electrode by the gas bubble may explain the data. However, this current density is high enough for Ni, Cu electrowinning. DSA® does not contaminate the electrolyte due to its resistance to acid and oxidation agent. In contrast, corrosion in the lead-
antimony anode was observed, probably due to the trace of chloride leaked from the ampholyte.

3.1.2. Cathode product from the two membrane electrowinning cell

A compact, smooth nickel product was obtained from the cathode at a current efficiency of more than 95% when the operating temperature was maintained at 50°C and the current density at 200 A/m². Due to the leakage of protons through the ACM anion exchange membrane, the pH of the catholyte decreased from 3.5 to 1.0. The pH change did not influence the cathode current efficiency when the pH of the catholyte was maintained higher than 0.8[6]. Meanwhile, the leakage of protons to the catholyte also compensated for the proton loss due to the hydrogen evolution at the cathode. It was not necessary to add boric acid as a buffer in the catholyte as has been previously reported[7].

3.1.3. Voltage-current curves in the membrane electrowinning cell

The cell voltage consists of cathodic plus anodic potentials, and the voltage drops over the membrane and the electrolyte. Figure 4 shows that the cell voltage increased linearly with the current density as well as with the voltage drop over the membrane and the electrolyte. The two lines seem parallel. The cell voltage is only about 2.8 volts at the current density 250 A/m², which is comparable to cell voltage from the common nickel electrowinning cell[8]. The voltage drop over the membrane and the electrolyte was obtained by subtracting the anodic potential and the cathodic potential from the total cell voltage, ignoring the IR drop from the circuit. When two calomel electrodes with lugging tubes were placed on the sides of a membrane, a voltage drop over the membrane was measured, which was in the range of 0.1 to 0.4 volts, depending on the current density.
Figure 2. Galvanostatic curve for DSA® during the electrowinning experiment.

Figure 3. Cyclic polarization curve for DSA® in 1.0 M H₂SO₄ solution.
3.2. Hydrochloric acid regeneration in the ampholyte

As reported in a previous paper[3], in the two membrane cell, protons from the water oxidation at the anode and the chloride due to the deposition of nickel at the cathode migrated to the ampholyte to satisfy the electric neutrality. This resulted in the regeneration of hydrochloric acid in the ampholyte. It has been reported that low initial concentration of the electrolyte resulted in a high cell voltage due to the low conductivity of the electrolyte and it took around 20 hours to reach an almost constant cell voltage in the batchwise test[4]. To perform the test work under a realistic condition, a solution of 0.2 M NiCl₂ and 0.5 M HCl was adopted as the initial ampholyte. The curve a in Figure 5 shows the acidity change in the ampholyte as function of time in the two membrane cell during nickel chloride electrowinning. Because part of the protons leaked to the catholyte and part of protons were detained in the anolyte, the acidity increase is not the expected straight line b shown in Figure 5. To regenerate a high concentration of hydrochloric acid in the ampholyte, the catholyte concentration should be increased in further test work. It has been reported that higher nickel concentration leads to a higher current efficiency of nickel electrodeposition and a lower cathode surface pH[9].

3.3. Chloride leakage through the cation exchange membrane

Theoretically, for a cation exchange membrane, only cations are mobile and can move freely under the influence of electric fields, concentrations, temperature and other differences in free energy. Anions are repelled by the membrane because of its fixed negative charges and the existence of Donnan-potential. Unfortunately, the selectivity of ion exchange membrane is effective only in dilute solutions not in a concentrated solution. Meanwhile, the chloride leakage direction is the same as the current direction, hence it is not surprising that certain amounts of chloride leak from the ampholyte to the anolyte. One has to try to reduce chloride leakage to an acceptable level (< 10⁻⁴ M).
3.3.1. The influence of the composition of the anolyte on the leakage rate of chloride

In previous work[3], it was observed that the chloride leakage rate is related to the amount of nickel transported through the cation exchange membrane. To depress nickel transport through the CEM, extra nickel ions were introduced into the anolyte. The composition of the anolyte is listed in Table 1. The chloride leakage rate through the CMS cation exchange membrane is shown in Figure 6. It can be seen that the leakage of chloride is not completely related to the extra nickel ion introduced in the anolyte. When pure nickel sulphate was used as the anolyte, the chloride leakage rate seems to become depressed. Chloride concentration in the anolyte reached an equilibrium. In contrast to what was expected, the chloride leakage rate through CMS seemed even higher when a mixture of 0.5 M H₂SO₄ and 0.5 M NiSO₄ was used as the anolyte as opposed to 1.0 M H₂SO₄ as the anolyte. This could be the result of a larger initial chloride concentration gradient existing between the anolyte and the ampholyte in experiment number 3.

![Graph showing voltage and voltage drop over the membrane and the electrolyte as function of current density.]

Figure 4. Cell voltage and voltage drop over the membrane and the electrolyte as function of current density.
3.3.2. Chloride leakage through other types of cation exchange membrane

It was presumed that the chloride leakage was related to the amount of nickel transported through the cation exchange membrane. In order to depress nickel ion transportation, the monovalent cation exchange membrane, CMS, was adopted for this work. Surprisingly, compared with the chloride leakage in Nafion-350, one of available multivalent cation exchange membranes, the chloride leakage rate is higher in the CMS membrane, as shown in Figure 7. Because bivalent nickel ions can not pass through the CMS membrane, chloride leakage is not proportional to the amount of nickel which transported through the cation exchange membrane. This indicated that the chloride leakage through the cation exchange membranes was not simply related to nickel transportation in the form of Ni\(^{2+}\), but as a complex of nickel chloride, such as [Ni(H\(_2\)O)\(_5\)Cl]\(^+\).
3.3.3. The application of silver ions for depressing chlorine evolution at the anode

Another way to avoid chlorine evolution at the anode could be the addition of silver ions to the anolyte. From the solubility product of silver chloride and silver sulphate,

\[ K_{sp} (\text{AgCl}) = 1.0 \times 10^{-10} \quad (25^\circ C) \]

\[ K_{sp} (\text{Ag}_2\text{SO}_4) = 7 \times 10^{-5} \quad (25^\circ C) \]

when \([\text{Ag}^+]\) is maintained \(10^{-5}\) M, in the anolyte of 1.0 M sulphuric acid (\(\text{H}_2\text{SO}_4 100\%\) dissociation to \(\text{SO}_4^{2-}\) assumed):

\[ [\text{SO}_4^{2-}] \times [\text{Ag}^+]^2 = 1.0 \times 10^{-10} << K_{sp} (\text{Ag}_2\text{SO}_4), \]

no \(\text{Ag}_2\text{SO}_4\) will precipitate in the anolyte, but the existence of \([\text{Ag}^+]\) in the anolyte will maintain chloride concentration

\[ [\text{Cl}^-] \leq \frac{K_{sp}(\text{AgCl})}{[\text{Ag}^+]} \leq 10^{-5} \text{ M} \]

Because the electrowinning was operated at \(50^\circ C\), more silver ions could be added into the anolyte without causing \(\text{Ag}_2\text{SO}_4\) precipitation. Figure 8 shows the chloride concentration change in the anolyte when \(1.5 \times 10^{-3}\) M \(\text{Ag}^+\) was added to the initial anolyte. In the first ten hours, chloride in the anolyte was removed effectively by the presence of \(\text{Ag}^+\), however, the chloride increased again in the anolyte after the consumption of silver ions in the anolyte by silver chloride formation. A white layer of silver chloride was observed on the membrane surface. It subsequently became grey and black due to the decomposition of silver chloride.
Table 1. The compositions of the ampholyte and the anolyte for chloride leakage comparison test.

<table>
<thead>
<tr>
<th>Experiment nr.</th>
<th>Composition of the initial anolyte</th>
<th>Composition of the initial ampholyte</th>
<th>Type of CEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 M H₂SO₄</td>
<td>0.2 M NiCl₂</td>
<td>CMS</td>
</tr>
<tr>
<td>2</td>
<td>1.0 M NiSO₄</td>
<td>0.2 M NiCl₂</td>
<td>CMS</td>
</tr>
<tr>
<td>3</td>
<td>0.5 M H₂SO₄ 0.5 M NiSO₄</td>
<td>0.2 M NiCl₂ 0.5 M HCl</td>
<td>CMS</td>
</tr>
</tbody>
</table>

Figure 6. Chloride leakage as a function of time with various anolytes.
Figure 7. The chloride leakage to the anolyte as a function of time for two types of cation exchange membrane.

Figure 8. The chloride concentration in the anolyte as a function of time when $1.5 \times 10^{-3}$ M Ag$^+$ was added in the initial anolyte.
3.3.4. Chloride leakage through double cation exchange membrane

From the above results, it would seem impossible to prevent chloride transport from the ampholyte to the anolyte completely. From our experimental work, it was learned that chlorine gas did not evolve at the DSA® anode when the chloride concentration in the anolyte was lower than 10^{-4} \text{ M}. Therefore, it was critical to maintain a chloride concentration below 10^{-4} \text{ M}. Although it was very difficult for one layer of the cation exchange membrane to stop chloride leakage effectively, it was expected that the chloride leakage would be substantially prevented when two layers of cation exchange membrane were adopted between the anolyte and the ampholyte.

![Graph showing chloride leakage over time](image)

Figure 9. Chloride leakage to the anolyte as a function of time when two cation exchange membranes were adopted between the anolyte and the ampholyte.

Figure 9 shows the chloride leakage to the anolyte through the cation exchange membranes when the Nafion-350 and CMS membranes were both used. The chloride leakage rate to the anolyte is much lower than when only CMS or Nafion-350 was used in the cell. To maintain a good electrical conductivity between the two cation exchange membranes, about 50 ml of solution with the same composition as the initial anolyte was introduced into
the space between the two cation exchange membranes. After 40 hours of electrowinning operation, the chloride concentration in this solution rose to 0.075 M. It appears practicable to pump out this small amount of solution from the cell and precipitate the chloride by silver ions and then circulate the solution back to the system. The removal of chloride by ion exchange columns could be an alternative.

4. CONCLUSIONS

In the two membrane electrowinning cell:

1) A lower, economically more attractive cell voltage was obtained due to the application of DSA® instead of the lead-antimony anode for oxygen evolution.

2) A compact, smooth nickel product was produced at the cathode in the two membrane electrowinning cell.

3) Chloride leakage is not very sensitive to the composition of the anolyte, but various types of cation exchange membrane showed different chloride leakage.

4) Silver ions could depress chlorine evolution from the anode, but is recommended that is used out of the anode compartment.

5) The installation of two cation exchange membranes between the anolyte and the ampholyte is effective in providing a lower chloride leakage.

5. REFERENCES:


Chapter 6

APPLICATION OF THE HYDROGEN DIFFUSION ANODE FOR THE REGENERATION OF HCl IN A MEMBRANE EQUIPPED ELECTROWINNING CELL

ABSTRACT:

The hydrogen diffusion anode developed for fuel cell application has been tested for the regeneration of hydrochloric acid instead of chlorine in the electrowinning of nickel chloride. The influence of chloride in the anolyte on the anodic potential was investigated. The relationship between, cell voltage and ion strength in the electrolyte, cell voltage and current density, current density and anode potential, and the cell voltage drop over the membrane and the electrolytes have been measured. Finally the possibilities for application of the hydrogen diffusion anode are 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 (nearly)closed circuit operation. In industrial nickel chloride electrowinning, for instance, metal is deposited at the cathode and chlorine is evolved at the anode. The by-product 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 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 our earlier work[2,3], the possibility of using a membrane cell and a dimensionally stable anode (DSA®) for the regeneration of chloride in the form of HCl during nickel chloride electrowinning has been investigated. In the present investigation, a
hydrogen diffusion anode developed for fuel cell application was adapted to achieve the regeneration of HCl at a low cell voltage, also during the electrowinning of nickel chloride.

2. HYDROGEN DIFFUSION ANODE

2.1. The gas diffusion anode

It has been reported that the exchange current density of H₂ oxidation on platinum surface can be in the order of 100 mA/cm² with a limiting current density of greater than 10⁴ mA/cm²[4]. Although this electrochemical reaction is fast on black platinum, a limiting current density was obtained due to the low solubility of hydrogen gas in aqueous solution in the order of 10⁻⁴ mole/l[5], which is not satisfactory for practical application. To overcome this problem, a sufficient amount of hydrogen should be transported to the surface of electrode. The simplest way is to introduce hydrogen gas directly at the surface of the anode instead of through the anolyte. A porous gas diffusion electrode was recommended to obtain a high mass transfer rate to active electrode site[6].

Porous electrodes offer two advantages over plane electrodes. The first is the reduction of the true current density for a given apparent or overall current density, reducing the surface overpotential as was first suggested in the late nineteenth century[7,8,9] In simple mathematical models of porous electrodes[10,11,12], the exchange current density, \( i_0 \), enters as the product \( A i_0 \) where \( A \) is the active electrode area per unit volume. If the exchange current density for a desired reaction is low, it might still be made to operate at an acceptable apparent current density and low overpotential by using a porous electrode with a large "\( A \)". The second advantage is an increased mass transfer rate. If an active species has a low solubility, such as hydrogen gas, high rates of mass transfer can be achieved by using a very large surface area electrode, once again a large value for \( A \).

A porous gas diffusion anode has been well discussed in some papers[13,14,15]. The early porous electrode was mainly developed for fuel cell application, i.e. for the
oxidation of hydrogen and reduction of oxygen. Attempts have also been made to find its application in electroplating and electrowinning of metal for the sake of energy saving[16,17], especially in zinc metallurgical industry, because the comparatively low market value of zinc causes the economic necessity of producing zinc at a low cost and a high recovery[18], but all work have been done were carried out in sulphate media. In this chapter, the mechanism of hydrogen oxidation, the structure of a porous gas-diffusion electrode and the processes occurring at the gas diffusion anode will be reviewed and discussed. Also new experimental data of the gas diffusion anode for hydrogen oxidation in chloride media , which is supposed to may deactivate the electrode, will be discussed.

PTFE-bonded platinized carbon porous electrodes are recommended for hydrogen oxidation in acidic media from fuel cell research. In this type of electrode, polytetrafluorethylene (PTFE) serves as a modern binder for carbon powders of many different types to produce porous electrode structures. Chemical stability is a feature which has singled out PTFE among other hydrophobic materials which have been used to produce gas-permeable and electrolyte repellent conductive electrode. Models for the structure and function of such a combination as platinum and PTFE have been described[19]. There is a considerable difference between a metal particle which is completely wetted by the electrolyte, has a small surface area (30 m²/g) and hardly any inner surface accessible. Carbon particles which are used in porous electrodes show a varying degree of hydrophobicility, have a large surface area (200-1000 m²/g) and the microstructure of the particle can be free or partially filled with electrolyte, depending on the interfacial tensions prevailing in the small pores.

A PTFE-bonded porous electrode generally consists of a catalyst, such as platinum, distributed in the form of small particles, in a porous substrate. In respect to an electrode structure and function, the typical electrode has three layers. Beginning from the electrolyte side, there are the following three layers to consider:

The first layer is a highly catalysed carbon layer which should not be too hydrophobic, otherwise it will not achieve a good interfacial contact with the
electrolyte as required. Due to the fact that PTFE-bonding is used, a certain repellency can not be avoided, even at low PTFE percentages (< 10%).

The second layer, often called “diffusion layer” has the purpose of transporting the gas with a minimum gas pressure drop to the wet catalysed carbon layer. This part of the electrode must be highly liquid repellent, a barrier against the penetration tendency of the electrolyte. It may contain 20 to 40% PTFE.

The third layer is the current collector. In alkaline fuel cell, a porous nickel sheet or a nickel screen impregnated with PTFE can be used as current collector. For acidic electrolyte graphite is one of the best candidate for the current collector.

The cross section of porous electrode is schematically shown in Figure 1.

![Diagram of porous electrode cross section]

Figure 1. The schematic of the cross section of porous electrode.

The hydrogen diffusion anode (HDA) used in the present test was prepared at ECN[20] by attaching the porous gas diffusion electrode (from E-TEK Inc.) to the Nafion-117 membrane, and adding a piece of graphite which served both as gas
conduit and current conductor. The stacking configuration of the HDA is shown in Figure 2. The geometric surface area of the gas diffusion electrode was 6.25 cm².

![Diagram of hydrogen diffusion anode](image)

Figure 2. Schematic cross section of the hydrogen diffusion anode.

The function of the cation exchange membrane is not only to prevent the hydrogen gas passing into the electrolyte, but also to protect the platinum catalyst from be poisoned by chloride. It has been reported that even a low concentration of chloride can reduce the platinum catalyst activity greatly[21]. It is therefore essential to isolate the platinum catalyst from the chloride solution. The membrane should also have high proton conductivity, low hydrogen permeability, adequate chemical and electrochemical stability.

2.2. Processes occurring in the HDA

During the hydrogen oxidation, a three phase interface is established in the region of the porous electrode, the electrolyte and hydrogen gas. The nature of this phase plays a critical role in the performance of hydrogen diffusion anode (DHA). The following processes are supposed to occur within the interior structure of HDA, a model was proposed by Yang[22],

- 1. Hydrogen molecule diffusion through backing material.
- 2. Hydrogen gas diffusion in the PTFE pores of the electrode.
3. Phase equilibrium between gaseous hydrogen and dissolved hydrogen at the surface of the water film covering the particles.

4. Dissolved hydrogen molecule diffusion across the water film to the surface of particles.

5. Adsorption of electroactive species onto electrode.

6. Electrochemical reaction in the agglomerate.

7. Transport of protons through the cation exchange membrane.

8. Transport of electrons in the solid phase of electrode.

Because the hydrogen gases have to diffuse through a thin electrolyte film that wets portions of the porous electrode to react electrochemically on the electrode surface, when the porous electrode contains an excessive amount of electrolyte, the electrode may "flood" and restrict the transport of gaseous species in the electrolyte phase. The consequence is a reduction in the electrochemical performance of the porous electrode. Thus a delicate balance must be maintained among the electrode, the electrolyte and the gaseous phase in the porous electrode structure.

2.3. Mechanisms of hydrogen oxidation

Compared with the extensively investigated hydrogen evolution reaction, the mechanism of the hydrogen oxidation reaction has been studied much less[23], but in the 1970s, there was an increasing interest on it, particularly with the renewed interest in fuel cells[24,25], due to the energy crisis in western countries. The mechanism of hydrogen oxidation is not necessarily identical to the mechanism of hydrogen evolution. Hydrogen evolution is observed at potentials where for most transition metals the electrode surface contains at least a monolayer of adsorbed hydrogen[26]. When hydrogen oxidation occurs in acid solution, the following mechanisms are generally proposed:

1.) The Volmer-Tafel mechanism:

\[
\begin{align*}
\text{H}_2 + 2\text{M} & \rightarrow 2\text{MH} & \text{(Tafel)} \\
2\text{MH} & \rightarrow \text{M} + 2\text{H}^+ + 2\text{e}^- & \text{(Volmer)}
\end{align*}
\]
and

2.) The Volmer-Heyrovsky mechanism:

\[
\begin{align*}
H_2 & \rightarrow MH + H^+ + e^- \quad \text{(Heyrovsky)} \\
MH & \rightarrow H^+ + e^- \quad \text{(Volmer)}
\end{align*}
\]

3.) Some investigators even have proposed another mechanism for the hydrogen oxidation [27]:

\[
\begin{align*}
H_2 & \rightarrow H_2^+ + e^- \\
H_2^+ + M & \rightarrow H^+ + MH \\
MH & \rightarrow M + H^+ + e^-
\end{align*}
\]

where M is the catalyst.

but this mechanism seems not thermodynamically feasible[28].

Relations between current density and electrode potential are presented for both the Volmer-Tafel and the Volmer-Heyrowsky mechanisms. It has been reported that the rate of electrochemical hydrogen molecule oxidation was shown to be equal to the rate of hydrogen dissociation measured in the gas phase for smooth platinum with equivalent coverage of hydrogen. These results indicate that the mechanism for electrochemical hydrogen molecule oxidation over smooth platinum in acidic electrolyte is slow dissociation of adsorbed hydrogen molecules to hydrogen atoms (Tafel reaction) followed by fast electrochemical oxidation of the adsorbed hydrogen atoms to protons (Volmer reaction).

3. EXPERIMENTAL DETAILS

The electrowinning of nickel chloride was carried out in a Perspex cell, consisting of two equal sized compartments clamped together and separated by an anion exchange membrane (AMH, from Tokoyama Soda), schematically shown in Figure
3. The solution volume of each compartment was 1000 ml and the effective dimensions were 10 x 10 cm. The electrowinning experiments were conducted at 50°C. The temperature was achieved by immersing the cell into a water bath. A potentiostat with CMS100 software (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. The cathode was a sheet of pure nickel. The anode is described below. The electrowinning was operated at an anode current density of 960 A/m² and a cathode current density of 200 A/m². The

![Diagram](image)

Figure 3. Cell arrangement for nickel chloride electrowinning of the membrane.

initial catholyte was 1.0 M NiCl₂ with 20 g/l H₂BO₃ added as an buffer to maintain the pH of the catholyte. The initial anolyte was 0.2 M NiCl₂. The cell voltage was measured by connecting a voltmeter to the anode and cathode. The cathodic current efficiency was determined by weighing the cathode before and after the electrowinning experiment. The experiments were conducted batchwise.

The hydrogen flow was controlled by means of a precision valve and a flow meter at the rate of 0.2 l/h.

The chloride concentration of the electrolytes was measured by titration with silver nitrate using dichlorofluorescein as the indicator. The nickel concentration was measured by AAS (Atomic Absorption Spectrophotometer Perkin-Elmer-AA275). The acidity of the anolyte was measured by titration with sodium hydroxide.
All chemicals were Merck chemical grade. The solutions were prepared by dissolving salt or diluting acid in distilled de-ionized water.

4. RESULTS AND DISCUSSION


The polarisation study of the hydrogen diffusion electrode was carried out with a 0.2 M NiCl₂ anolyte to observe its electrochemical behaviour. As depicted in Figure 4, a large current can be obtained from the hydrogen oxidation at low electrode potential under these conditions. An eleven days experiment showed that the hydrogen diffusion anode worked stably in chloride solution, see Figure 5. Limited by the capacity of the potentiostat, the maximum current density obtained from the present experiment was 1200 A/m².

4.2. Cell voltage

4.2.1. Influence of electrolyte composition

As depicted in Figure 6 the cell voltage was related to the ionic strength of the electrolyte. The ionic strength is calculated by

\[ I_{(m)} = \frac{1}{2} \sum m_i \times z_i^2 \] (8)

where \( I_{(m)} \) is the ionic strength, \( m_i \) and \( z_i \) signify the molar concentration and charge number of the relevant ion in the anolyte respectively. Because the initial concentration of the anolyte is relatively low, the low conductivity of the anolyte resulted in a high cell voltage. The series 1, 2, 3 are the contribution of nickel ions, chlorides and protons to the ionic strengths respectively in the anolyte. The conductivity of the anolyte increased as the electrowinning proceeded due to the increase of proton concentration from the oxidation of hydrogen at the anode and the increase of chloride concentration migrated from the catholyte, hence it is important to maintain a high enough ionic strength in the electrolyte to reduce the cell voltage.
Figure 4. Cyclic polarisation curve of HDA in 0.2 M nickel chloride at 50 °C.

Figure 5. Anodic potential as a function of time in 1.0 M HCl solution at a anodic current density of 250 A/m².
Figure 6. The cell voltage as a function of ionic strength during the electrowinning of nickel chloride.

4.2.2. The influence of the current density on the cell voltage and electrode potential

In the described experiments, the anodic current density was different from the cathodic current density. Figure 7 shows the influence of anode current density on the total cell voltage. The cell voltage consists of the cathodic potential, the anodic potential, and the voltage drops over the membrane and the electrolyte. The cell voltage and the anodic potential increased linearly when the current density increased. It can be seen from Figure 7 that the slope for the anode potential line is lower than that of cell voltage. A high anodic current density can reduce the investment in HDA’s, but a high cell voltage will increase the power consumption. These two parameters should be economically optimised.

4.3. The performance of the anion exchange membrane

In order to maintain a relatively stable pH in the catholyte, it is necessary to keep the acid regenerated by oxidation of hydrogen separated from the catholyte. A high acidity in the catholyte will result in a low cathode current efficiency. From the
chloride concentration increase in the anolyte, the operation period and the current flux through the membrane, the anion transfer number can be calculated as follows:

\[ t_i = \frac{z_i \times j_i}{\sum z_i \times j_i} \]  \hspace{1cm} (9)

where \( t_i \), \( Z_i \) and \( J_i \) are the transfer number, charge number and flow rate of the related ion respectively.

![Graph showing cell voltage and anode potential as a function of current density.](image)

**Figure 7.** The cell voltage and anodic potential as a function of anodic current density.

The chloride transfer number for anion exchange membrane AMH is 0.87. It means that 13% of current is carried by the cations, especially by the transport of protons through the AMH membrane. This is consistent with the pH decrease from 3.5 to 0.75.

The voltage drop over the membrane is another important parameter. In these experiments, the total voltage drop over membrane and electrolytes was measured by subtracting the anodic potential and cathodic potential from the total cell voltage, instead of measuring the voltage drop over the membrane directly. Figure 8 shows the combined voltage drop over membrane and electrolyte as function of current.
density. It increased linearly with the current density across the membrane. This is consistent with Ohm’s law.

Figure 8. The additional voltage drop over membrane, circuit and electrolyte as a function of current density.

Figure 9. The concentration of chloride and proton in the anolyte as a function of operational time.
4.4. Regeneration of HCl in the anolyte

As the electrowinning proceeded, the acidity of the anolyte increased linearly as function of time due the oxidation of hydrogen. The chloride concentration increased linearly as well as function of time as shown in Figure 9. The HCl concentration obtained from the electrowinning experiment reached 1.0 M. The hydrochloric acid concentration does not influence the performance of the hydrogen diffusion anode when its concentration increases from one molar to three molar another testwork has learned.

5. CONCLUSIONS:

1) Hydrochloric acid was generated by the use of a hydrogen diffusion anode in nickel chloride electrolysis.

2) By attaching a cation exchange membrane to the HDA, poisoning of the platinum catalyst by chloride was not observed over a test period of eleven days.

3) The HDA has a very favourable current density vs. voltage characteristics.

6. REFERENCES:


5. Chapter 1 in this thesis


Chapter 7

The Mechanism and Electrocatalysis of Chlorine Evolution

1. INTRODUCTION

The history of elemental chlorine is relatively short, embracing less than two hundred years; yet the story of chlorine compounds reaches far back into prehistoric times. The early history of chlorine is shown as follows:

1300  Presumably first observation of chlorine gas.
1772  Preparation of chlorine gas. Definition of chlorine as dephlogisticated muriatic acid.
1798  First patent on chlorine bleaching solutions.
1800  Decomposition of hydrogen chloride by electric sparks.
1801  Development of chlorine generator for sanitation purposes.
1809  Consideration of element character for chlorine.
1810  Definition of chlorine as a chemical element—hydrate character ascertained for chlorine hydrate.
1815  General acceptance of element character for chlorine.
1823  Quantitative determination of the composition of chlorine hydrate installation of disinfecting equipment using chlorine in hospitals.
1826  Chlorine water used in obstetric wards for the prevention of puerperal fever.
1831  Fumigation with chlorine during the great European cholera epidemic.

The first patent connected with any industrial use of chlorine, dated 1799, was for its use in bleaching. During the last half of the nineteenth century, the demand for chlorine for bleaching grew at a rate that brought about the invention and development of processes for chlorine production. The first commercial production of chlorine was started in Germany in 1888 by the
Griesheim Company, as a by-product of KOH manufacture. Nowadays, the annual world production of chlorine is around \(4 \times 10^7\) tons and more than 99% of commercial chlorine is produced electrolytically.

More specifically, chlorine is produced commercially by the electrolysis of an alkali metal chloride brine, such as a sodium chloride brine, with the corresponding alkali metal hydroxide also being produced as a result of the electrolysis. Until the middle of 1970's, two different types of electrolytic cell were used to effect this electrolysis, i.e. diaphragm and mercury cells. They are distinguished mainly by the purity of metal hydroxide produced and production efficiency. A high purity of caustic can be produced with mercury cell, i.e. the foreign anion concentration is less than 0.05% of the concentration of hydroxide.

In the diaphragm cell, the catholyte is separated from the anolyte by a liquid permeable diaphragm, generally constructed of asbestos. The sodium hydroxide is recovered in a mixture of sodium chloride, called “cell liquor”. This catholyte or cell liquor normally contains about 11% sodium hydroxide and 14% to 15% sodium chloride, which must be removed from sodium hydroxide. The separation is realized by evaporation of the cell liquor to a concentration of about 50% sodium hydroxide with the sodium chloride concentration ranging from 0.8 to 2.0%, depending on the temperature of sodium hydroxide solution.

The method of producing chlorine and caustic alkali in an electrolytic cell with a mercury cathode was first patented in 1882[1]. After half a century of development and improvement, the cell capacity was expanded to 200,000 amperes. In the mercury cell, chlorine gas is evolved at the anode, and alkali metal is deposited at the surface of mercury cathode, in which it dissolves to form a liquid amalgam. Followed by decomposing the amalgam with water, a concentrate sodium hydroxide ranging up to 70% and hydrogen gas are produced, the mercury is recycled to the cell for reuse as the cathode.
The choice between the diaphragm process and mercury process was mainly a question of whether solid or strong brine is cheaper, and of the purity of the caustic produced. Mercury process requires solid salt for resaturation of the partly depleted brine from the electrolysis and can supply superior quality 50% NaOH directly, as against the weak and impure caustic liquor. On the other hand, mercury cells require about 15% more energy per ton of product than diaphragm cells.

Since end of 1970', a new type of electrolytic cell, i.e. ion exchange membrane cell has been introducing to chlor-alkali industry yielding high concentration and purity of caustic, with low energy consumption.

In this chapter, possible mechanisms of chlorine evolution and the performance of various types of electrocatalyst for chlorine evolution will be reviewed and discussed.

2. THE MECHANISM OF CHLORINE EVOLUTION AT THE ANODE

The chlorine evolution reaction, \( 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e \)
can be generalized as a simple two step reaction \( \text{A} + 2e \rightarrow \text{C} \), proceeding heterogeneously through the formation of intermediate \( \text{B} \)

\[
\text{A} \xrightarrow{h} \text{B} \xrightarrow{h} \text{C}
\]

Figure 1 depicts the energy curve for above reaction. According to such a simple picture, it is seen that a modification in the energy state of \( \text{B} \) with the conditions of \( \text{A} \) and \( \text{C} \) remaining invariant leads to a change in the activation energy of both steps.
Figure 1. Simplified energy diagram to illustrate the effect of adsorption of intermediate B on the activation energies for the various steps of the process.

There are two mechanisms widely accepted for the chlorine evolution reaction at RuO₂:

Pathway I
1) \( M + Cl^- \rightarrow MCl + e \)
2) \( MCl + MCI \rightarrow 2M + Cl_2 \)

and Pathway II
1) \( M + Cl^- \rightarrow MCl + e \)
3) \( M-Cl + Cl^- \rightarrow Cl_2 + M + e \)

where M is the active site of a electrocatalyst.

These mechanisms are analogous to the so-called Volmer-Tafel and Volmer-Heyrovsky mechanisms of the hydrogen evolution reaction, respectively. The formation of adsorbed chloride as the first step is common to both mechanisms I and II. Hence, when it is the rate-determining step, one cannot distinguish between the two mechanisms. It is, however, possible to recognise that step (1) determines the rate. The rate of reaction may be written as:
\[ \vec{V} = k_{(1)} c_{cr} (1 - \theta) \]  \hspace{1cm} (1)

Where \( \vec{V} \), \( k_{(1)} \) are reaction rate and rate constant for step (1) in forward reaction, potential-dependent because the reaction involves the transfer of an electron. The equation reflects the fact that the rate of step (1) is first order in chloride and the amount of surface still available for chloride adsorption.

In the situation where step (1) is much slower than step (2) or (3), the rate of removal of adsorbed chloride must be rapid compared to its formation and the absorbed chloride cannot be present at high coverage. Therefore, \((1 - \theta)\) must be close to one and a very simple expression may be written for the reaction rate or current density.

\[ \vec{V}_{(1)} = k_{(1)} c_{cr} \]  \hspace{1cm} (2)

and the current density for chloride evolution is given by:

\[ j = F k_{(1)} c_{cr} \theta = F k_{(1)} c_{cr} \exp\left(\frac{\alpha F}{RT} - E\right) \]  \hspace{1cm} (3)

where \( k_{(1)} \) is the value of \( k_{(1)} \) at \( E = 0 \). Throughout this discussion of the chloride evolution reaction, we shall assume that for each elementary reaction, \( \alpha_A + \alpha_C = 1 \) and we shall write the anodic transfer coefficient \( \alpha_n \) where \( n \) is the reaction concerned. Equation (3) may be converted to the form:

\[ \log j = \log F k_{(1)} + \log c_{cr} + \frac{\alpha_n F}{2.3RT} E \]  \hspace{1cm} (4)

or

\[ \log j = \text{constant} + \log c_{cr} + \frac{\alpha_n F}{2.3RT} E \]  \hspace{1cm} (5)
and it may be seen that the reaction is first order in chloride and if \( \alpha_1 = 0.5 \), then the Tafel slope is:

\[
\frac{\partial E}{\partial \log j} = \frac{1}{120} mV
\]  

(6)

In pathway I, with step (2) as the rate determining step, the rate of step (2) is given by

\[
V_{(2)} = 2 \vec{k}_{(2)} \theta^2
\]  

(7)

where \( \vec{k}_{(2)} \) is a chemical rate constant and, therefore, independent of potential. The factor 2 is necessary because two adsorbed chloride atoms are lost every time the reaction occurs once. The current density for chlorine evolution when step (2) is the rate determining step is, therefore,

\[
j = 2F \vec{k}_{(2)} \theta^2
\]  

(8)

The coverage of the surface by chloride atoms may be found by noting that

\[
\frac{d\theta}{dt} = \vec{k}_{(1)} c_{Cl} (1 - \theta) - \vec{k}_{(1)} \theta - 2 \vec{k}_{(2)} \theta^2
\]  

(9)

and using the steady state approximation, \( \frac{d\theta}{dt} = 0 \), one obtains

\[
\vec{k}_{(1)} c_{Cl} (1 - \theta) - \vec{k}_{(1)} \theta - 2 \vec{k}_{(2)} \theta^2 = 0
\]  

(10)
This equation still remains somewhat intractable but in a range of practical conditions where step (2) is slow, the final term is insignificant, i.e. we can treat step (1) as a pre-equilibrium to the rate-determining step, step(2). Then

\[ \vec{k}_{(i)} c_{cr} (1 - \theta) = \vec{k}_{(i)} \theta \]  
(11)

Including the potential dependence of the two rate constants \( \vec{k}_{(i)} \) and \( \vec{k}_{(i)} \) leads to

\[ \vec{k}_{ii} \exp(\frac{\alpha_i E}{RT}) c_{cr} (1 - \theta) = \vec{k}_{ii} \exp(\frac{(1 - \alpha_i) E}{RT}) \theta \]  
(12)

and hence

\[ \theta = \frac{K_i c_{cr} \exp(\frac{F}{RT} E)}{1 + K_i c_{cr} \exp(\frac{F}{RT} E)} \]  
(13)

where \( K_i \) is the ratio of rate constants, \( K_i = \frac{\vec{k}_{ii}}{\vec{k}_{ii}} \). Close to the equilibrium potential \( K_i c_{cr} \exp(\frac{F}{RT} E) \ll 1 \) and, therefore,

\[ \theta \approx K_i c_{cr} \exp(\frac{F}{RT} E) \]  
(14)

The \( j \) vs. \( E \) relationship may be obtained by substituting into equation (8), i.e.

\[ j = 2F \vec{k}_i K_i^2 c_{cr}^2 \exp(\frac{2F}{RT} E) \]  
(15)
and:

\[
\log j = \log 2 F k_2 K_1^2 + 2 \log c_{cr} + \exp\left(\frac{2F}{RT} E\right) \tag{16}
\]

for this mechanism and in this potential range, it can be seen that current density varies as the square of chloride concentration and the Tafel slope is 1/30 mV.

In pathway II, when step (3) is the rate-determining step

\[
\vec{V}_{(3)} = k_{(3)} c_{cr} \theta \tag{17}
\]

since it depends on the concentration of chloride and the fraction of surface covered by M-Cl species, \(k_{(3)}\) is again potential dependent because the reaction involves the transfer of an electron. The current density when step (3) is the slow step is then given by

\[
j = F k_{(3)} c_{cr} \theta \tag{18}
\]

Two limiting forms of the rate expression are possible at low and high overpotentials.

a) At low overpotentials, both \(\vec{V}_{1}\) and \(\vec{V}_{1}\) are much faster than \(\vec{V}_{3}\) and \(\theta\)

\[
j = 2F k_{31} \exp\left(\frac{\alpha_3 F}{RT} E\right) c_{cr} K_1 c_{cr} \exp\left(\frac{F}{RT} E\right) \tag{19}
\]

\[
j = 2F k_{31} K_1 c_{cr}^2 \exp\left(\frac{1+\alpha_3 F}{RT} E\right) \tag{20}
\]
For this mechanism, it can be concluded that the reaction is second order in chloride and the Tafel slope is 1/40 mV when $\alpha_3 = 0.5$.

b) At high overpotential, $\vec{V}_3 \gg \vec{V}_1$ and $\vec{V}_1 = \vec{V}_3$, hence:

$$\vec{k}_{31} \exp(\frac{\alpha_1 F}{RT} E)c_{c_l} (1-\theta) = \vec{k}_{31} \exp(\frac{\alpha_3 F}{RT} E)c_{c_r} \theta$$ (21)

if $\alpha_1 = \alpha_3$, and $\theta \to 1$, in this potential range, the current density follows the equation,

$$j = 2F \vec{k}_{31} c_{c_r} K \exp(\frac{\alpha_3 F}{RT} E)$$ (22)

and

$$\log{j} = \log{2} + \log{k}_{31} + \log{c_{c_r}} + \alpha_3 \frac{F}{2.3RT} E$$ (23)

The current density again is first order in chloride and gives a Tafel slope of 1/120 mV. The change in Tafel slope from 1/40 mV at low overpotential to 1/120 mV at high overpotentials has been observed on platinum[2]. It was found that Cl$_2$ evolution is controlled by the rate of recombination of discharged Cl radicals at Pt, Au oxidised Ru electrodes as shown in step(2), pathway I[3,4,5].

3. ELECTROCATALYSIS OF CHLORINE EVOLUTION-ANODE MATERIALS

3.1 Graphite

Although graphite has been the main "insoluble" anodic material in the chloralkali industry world wide for a very long time due entirely to its excellent
properties[5,6], such as high chemical resistance, good conductivity, considerable mechanical strength, high surface to volume ratio and importantly low price, some consumption does in fact take place, primarily due to the chemical attack by "active" oxygen generated during electrolysis, but also to the highly oxidising nature of the product — chlorine[7,8,9]. The consumption of graphite is, approximately 3 kg/tonne of chlorine in a diaphragm cell and 2 kg/tonne in a mercury cell[7]. Graphite oxidation results in the formation of chlorinated hydrocarbons and CO\textsubscript{2}, contaminating the produced Cl\textsubscript{2}, and in dimensional changes of the anode, which requires adjustment of the electrode position and periodic replacement of the anode.

Much research has been carried out to determine the graphite corrosion mechanism[8,9,10], the effect of electrolysis variables[11], and possible ways of reducing the consumption[12]. The presence of carbon dioxide and, to a lesser extent, carbon monoxide in the anode gas and the formed graphite sludge show that the anode is attacked were both chemically and mechanically. Graphite anodes are porous disperse bodies which consist of interconnecting carbon crystals, 70-80% of its volume consisting of solid material, the remaining being pores[13]. The mechanism of chemical attack to the anode is not simple due to the porous nature of the graphite, and it is easier to consider external and internal attack separately. The internal attack occurring within the pores weakens the intercrystalline bonds causing graphite particles to spill off and resulting chiefly in mechanical consumption. Vaaler [14] suggests that external attack of graphite anodes occurs by rapid adsorption of oxygen followed by a conversion to chemisorbed oxygen, which is then rapidly desorbed, breaking a carbon bond, to give carbon monoxide.

3.2. Metals and Oxides

Facing the problems with graphite anodes, better anode materials were requested by the industry. Technically, precious metals, such as platinum, are quite satisfactory, but their high price constitutes a bar to their being used on a large scale. In order to obviate the drawback of the high price of precious metals, it was recommended to use an anode consisting of a substrate of a
less precious or base metal, coated with a layer of precious metal. H.B. Beer found that titanium is particularly suited to be used as a core metal substrate for the an anode, because it appears that titanium is not only capable of forming a barrier layer in aqueous solutions of virtually all electrolytes (whereas other metals such as bismuth, tantalum and zirconium will only do this if oxygen is evolved directly at the anode), but also because in addition a very stable barrier is formed which is resistant to oxygen and which upon prolonged use continues to perform its function.

Because of the relatively high anodic potentials involved, chlorine evolution takes place on an oxide film on most metal substrates. In the case of noble metals, e.g. Pt, such films are in the range of monolayer or submonolayer dimensions. Therefore, it is often the properties of the oxide rather than those of the metal which determine the kinetics of chlorine evolution[3]. After titanium was widely accepted as a substrate material, the attention has been directed to the function of oxide film in the chlorine evolution.

Owing to the success of RuO$_2$ -based DSA$^\circ$ electrode in the chlor-alkali industry, a significant amount of study has been carried out on the kinetics and mechanism of chlorine evolution over the past 30 years or so. A considerable body of experimental data has therefore been accumulated regarding the chlorine evolution reaction at RuO2 electrodes, which includes E vs. log j plots, reaction order determinations, pH dependence studies, impedance measurements, and XPS studies of electrodes before and after chlorine evolution experiments. In general, the Tafel slope value has been found to be independent of chloride concentration.

The possibility of involvement of oxygenated species in the intermediate stages of Cl$_2$ evolution were discussed by Burke and O'Nell[15] and Ausgustinski et al. [16]. Burke and O'Neill proposed a modified Volmer-Hayrovsky scheme for RuO2

$$O_{ads} + Cl^- = OCl_{ads} + e$$
\[ \text{OCl}_{\text{ads}} + \text{Cl}^- = \text{O}_{\text{ads}} + \text{Cl}_2 + e \]

The \( \text{O}_{\text{ads}} \) species could actually be RuO\(_3\). Augustinski et al. concluded that RuO\(_3\), as well as two different chloride species, were present on the surfaces of RuO\(_2\) and RuO\(_2\)/TiO\(_2\) electrodes which had been used as anodes for chlorine evolution. These authors suggested that Ru(VI) species may play a role in the chlorine evolution process and concluded that reaction sequences such as warranted consideration.

\[ 2\text{Cl}^- + \text{RuO}_3 + 2\text{H}_3\text{O}^+ \rightarrow (\text{RuO}_2)\cdot 2\text{Cl}_{\text{ads}} + 3\text{H}_2\text{O} \]

\[ \text{RuO}_2 + 3\text{H}_2\text{O} \rightarrow \text{RuO}_3 + 2\text{H}_3\text{O}^+ + 2e \]

It has been claimed that the formation of mixed crystal of metal oxides in the active layer is one of the factors determining the efficiency of these electrodes\([17,18]\). Overpotential has yet been reported to increase\([19,20,21]\) as the RuO\(_2\) content decreases in RuO\(_2\)/TiO\(_2\) electrodes. Pure RuO\(_2\) has always been observed to be the best electrocatalyst from the kinetic point of view. The activity of RuO\(_2\)/TiO\(_2\) electrodes for chlorine evolution decreases only slightly on decreasing the RuO\(_2\) content from 100 down to 20-30%\([22]\), at which point a rapid fall off with further decrease in RuO\(_2\) content occurs. This critical composition is apparently associated with the appearance of another phase, anatase, in the oxide layer.

Only a few studies are available on chlorine evolution on oxide electrodes other than RuO\(_2\) based electrodes, if some mentions in the patent literature are excluded. For the purpose of comparison, the performance of lead oxide, magnetite, cobalt spiel, manganese dioxide, platinum and iridium dioxide for chlorine evolution will be briefly reviewed here.

Fe\(_3\)O\(_4\) has been subjected to investigation as a possible anode material since the beginning of this century. Magnetite Fe\(_3\)O\(_4\) was used in chlorine technology before the introduction of graphite\([23,24,25]\) but it is not attractive.
because of its fragility, difficult workability, high overpotential[26]. Further, the electrical characteristics[27,28] are not suitable for very high current densities.

Lead dioxide may be used in the form of an electrodeposit on a suitable substrate such as graphite[29]. This oxide is stable under such conditions and resistant to acids. The high overpotential for oxygen evolution[30,31] at β-PbO₂ make this material suitable for chlorate production[29, 32]. PbO₂ is a poor electrocatalyst, however, for chlorine evolution[33]. At a high current densities the overpotential for chlorine evolution at PbO₂ is higher than at graphite[23].

Because of its inexpensive nature and widespread use as a cathode in batteries, MnO₂ has been extensively studied from the viewpoint of its physico-chemical properties and its cathodic behaviour. Good performances have also been observed with MnO₂ based electrodes for chlorine evolution prepared by thermal decomposition of manganous nitrate. It was found that MnO₂ films on Pt as well as Ti with a RuO₂ interlayer worked well[34]. Ti alone is not a suitable substrate because MnO₂ cannot dope TiO₂. Much higher overpotentials are observed[35] with massive MnO₂ electrodes as well as with an active layer on graphite. The drawback of MnO₂ coated electrodes is that potential was observed to increase with time as a consequence of change at both the film/substrate interface and film/electrolyte interface. The anode corrosion may take place mainly through the dissolution

$$\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$$

Good performance is obtained with cobalt oxide electrodes provided some precautions are used[36]. The pre-treatment of the Ti support material has a great influence on the final behaviour. The temperature of formation of the active layer from nitrate between 160 and 350°C has no influence on the E-log j relationships, where j is current density. However, if it is increased to 400 and 460°C, the curve are bent upwards. Such a behaviour disappears if a RuO₂ interlayer is used. A Tafel slope of 40 mV decades⁻¹ was found for
chlorine evolution at Co$_3$O$_4$ along with reaction order of 1 respect to Cl$^-$ ion[36].

The evolution of chlorine on a number of oxide electrodes such as PdO, PtO$_2$ and IrO$_2$ have been investigated by Tamura and his co-workers[37,38]. In terms of overpotential, Tamura's sequence is RuO$_2$ < PtO$_2$ < IrO$_2$ < MnO$_2$. These results include the surface area contribution and are more relevant to direct practical appraisal of the electrocatalytic activity.

Figure 2. Overpotential for oxygen evolution as a function of enthalpy change for the lower $\rightarrow$ higher oxide transition.

Electrocatalysis is essentially still an experimental branch of electrochemistry. Due to the influence of the preparation procedure on the electrocatalytic activity it is very difficult to disentangle the various parameters which are simultaneously affected. However, the essence of electrocatalysis is to establish a predictive basis for the design and optimisation of catalysts. In catalysis with oxides, in particular in oxidation reactions involving oxygen and chlorine evolution, the strength of oxygen adsorption is generally regarded as determining the catalytic activity[39,40,41], since the chlorine or oxygen molecule must pass through a dissociation step to become active. Although the nature of intermediates in the chlorine evolution reaction is not unambiguously
identifiable, the interaction of the surface with oxygenated species is thought to be the determining factor. In Figure 2 the relationship between the standard enthalpy of M(III) to M(IV) oxide transition and the overpotential of oxide to oxygen evolution is given. This relationship is similar to that between the exchange current density for hydrogen evolution and the strength of metal-hydrogen bond formed in the electrodes. This may explain the electrocatalytic activity of RuO$_2$ for the evolution of chlorine.

4. REFERENCES:

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Chapter 8

ELECTROOXIDATION OF HYDROGEN CHLORIDE TO CHLORINE IN A MEMBRANE EQUIPPED CELL
PART I: CATHODE POTENTIAL

1. INTRODUCTION

When hydrogen in organic compounds is substituted by chlorine, half the chlorine is converted into hydrogen chloride and is thus lost to chlorination. The gaseous hydrogen chloride formed is normally absorbed in water or dilute hydrochloric acid to produce strong hydrochloric acid. Demand for strong hydrochloric acid has not been developing fast enough to keep up with the supply. Shipments over long distances are not economical because freight charges are high on a material that is roughly two-thirds water. This situation makes it desirable to consider new means of producing chlorine from strong hydrochloric acid.

Regeneration of chlorine from hydrogen chloride may be achieved by four methods:

(1) Oxidation of HCl by oxygen in the presence of a catalyst, e.g. the Deacon Process using a liquid catalyst.
(2) Oxidation of HCl by NO₂.
(3) Electrolysis of HCl with production of chlorine and hydrogen.
(4) Indirectly, via electrolysis of metallic chloride solutions.

Of these four methods, the third is preferred because of the simplicity of equipment and of operation, as well as the relatively low capital cost.

Development of direct electrolysis of hydrogen chloride was conducted initially at Bitterfield in the I.G. Farben Company[1], followed by G. Messner and his collaborators, and finally realised by De Nora in 1956[2]. The first HCl
Electrolysis cell was constructed with vertical bipolar electrodes and with anodes of lump graphite. Attempts have also been made to reduce metal ions from a higher to a lower valence in the electrolyte solution, for example, ferric to ferrous or cupric to cuprous [3,4,5], instead of producing hydrogen gas at the cathode, e.g. the electrolysis of metallic chloride solution. Such valence reduction occurs at a voltage lower than that for the cathodic evolution of hydrogen gas. The consumption of energy is reduced. A drawback of this mode of operation, however, is that the metal ions of low valence, which have been formed and separated only by a diaphragm from the anolyte, can be re-oxidised at the anode, through which loss of current efficiency occurs. Installing a (semi)permeable diaphragm helps as a barrier, except that all precipitation reactions due to the redox product (such as for MnO₂), occur in the diaphragm, and plugging may result. Also, since the electrolyte passes from the anode compartment to the cathode compartment, the electrolyte composition in the entire circuit is more or less the same. It is not possible to take advantage of different anolyte and catholyte compositions, to meet the needs of the process. Separation of cathode and anode by a ion exchange membrane would overcome these shortcomings. No work on this approach has been found reported in the literature.

In the present Chapter, electrolysis of hydrogen chloride was conducted in a membrane cell with either ferric or cupric reduction as the cathodic reaction. The electrode potential has been investigated as a function of electrolyte composition, current density and electrolyte agitation situation.

2. EXPERIMENTAL DETAILS

The experimental set-up with two separate circuits of solution, the anodic and the cathodic circuit, is schematically shown in Figure 1. The perspex electrolysis cell was divided by an ion exchange membrane into anode and cathode compartments. The volume of each compartment was 314 millilitres and the surface of the membrane was 7850 mm².
The anodic circuit contains an anode compartment, a gas-liquid separator for the chlorine gas and spent electrolyte separation and a reservoir for the anolyte. The cathodic circuit consists of a cathode compartment, means for ferrous reoxidation and a reservoir for the catholyte. The reservoirs are immersed in a water bath to maintain the electrolyte temperature at 50°C. A constant air flow was maintained through the external catholyte to reoxidise the ferrous ions. The thermostated solutions in both circuits were pumped upwards through the cell by peristaltic pumps.

![Diagram of electrolysis setup](image)

Figure 1. The schematic representation of the set-up for electrolysis of hydrogen chloride.

A DSA® disc from Magneto-Chemie B.V., the Netherlands, a titanium substrate coated with ruthenium and titanium oxide mixture, was used as the anode, which was placed against the back wall of the anodic compartment at a distance of 35 mm from the membrane. The cathode was a titanium disc with a platinum coating, also from Magneto-Chemie B.V. The surface area of both the anode and cathode was 3850 mm², half the membrane surface area. A saturated calomel electrode (SCE) was used as the reference electrode.
The electrolyses were carried out galvanostatically, using an E015-20 Delta Electriika power supply. The cell voltage was measured by connecting a voltmeter to the anode and the cathode.

All chemicals were Merck chemical grade. The solutions were prepared by dissolving the salts or diluting the acid in distilled de-ionised water.

3. RESULTS AND DISCUSSIONS

3.1. Polarisation behaviour of the anode

Figure 2 shows that the anodic potential increases linearly as the current density increases. The slope of the line is consistent with that reported in the literature[6]. Compared to brine electrolysis, the acidity of the anolyte is much higher, but no corrosion of the anode was observed in the photomicrograph comparison after two months of operation.

![Figure 2. Polarisation curve for chlorine evolution at a DSA® in 2.2 M HCl solution, 50 °C.](image-url)
3.2. Evolution of hydrogen at the cathode

In order to minimize energy consumption, an electrode potential as low as possible is preferred for a given electrolysis process at a certain current density. As mentioned above, the anodic potential in the chlorine production can hardly be improved. Attention will therefore be mainly focused on the reduction of the cathode potential. Figure 3 shows the polarisation curve for hydrogen evolution on the platinized titanium electrode in 5.0 M hydrochloric acid solution. There is a considerable overpotential for hydrogen evolution at high current densities. Because hydrogen is not always a profitable product, it might be economic to adopt a half reaction which possesses a lower cathodic potential than H⁺/H₂, such as Fe³⁺/Fe²⁺. Thermodynamically, there is at least a 0.77 V advantage when introducing Fe³⁺ → Fe²⁺ as the cathodic reaction instead of hydrogen evolution.

Figure 3. Polarisation curve for hydrogen evolution on a platinized titanium electrode in 5.0 M HCl solution, 50 °C.
3.3. Metal ion reduction at the cathode

3.3.1. Ferric reduction

Ferric to ferrous reduction was the first system to be considered as a substitute for hydrogen evolution because of the considerable differences in the standard redox potential and the easy reoxidation of ferrous. Figure 4 shows that in all cases, the cathode potential became negative as the current density increased when various concentrations of ferric chloride solution were used as the catholyte. Because of the low overpotential for hydrogen evolution on platinum electrode, it was assumed that the current was due to both hydrogen evolution and ferric reduction at potentials below 0.0 V. Therefore, the cathode current density at zero volts of electrode potential is defined as the limiting current density of metal ion reduction. The limiting current density was used to evaluate a polyvalent metal ion pair, i.e. a polyvalent metal ion pair which has a large limiting current density for its reduction without hydrogen evolution is desired. In Figure 4, it is obvious that a higher limiting current density was reached when a higher concentration of ferric chloride solution was used as the catholyte. For catholytes containing 0.5 M, 1.0 M and 2.0 M FeCl₃, the limiting current densities at 50 °C are about 400, 650 and 900 A/m² respectively.

In Figure 4, all potential-current density (E - j ) curves can be divided into three sections. The low current density section and the high current density section, both with a low slope value, are separated by a steeper section where the diffusion of reactants to the surface of electrode is rate limiting. In the high current density section the electrode reaction is mainly hydrogen reduction. Addition of hydrochloric acid to the catholyte did not result in a higher limiting current density as shown in Figure 5.
Figure 4. The cathode potential as a function of current density with various concentrations of ferric chloride as the catholyte at a platinized electrode, 50 °C.

3.3.2. Cupric reduction as the cathodic reaction

Judging by the standard redox potential of $\text{Cu}^{2+}/\text{Cu}^+$ (0.152 V), it appears to offer very little advantage for the cathode reaction. However, because this reaction is carried out in chloride medium, the formation of a cuprous complex will favour the cupric reduction. In Figure 6, it can be seen that the redox potential for $\text{Cu}^{2+}/\text{CuCl}_2^-$ is more than 0.5 volts and that no copper metal will be produced until the cathode potential reaches 0 volts when chloride activity is higher than 5.0 M. This suggests that the reduction of cupric to cuprous chloride complex as the cathode reaction, instead of proton reduction, may be favourable.

Using the same platinized titanium cathode and test conditions, a similar result for the ferric solution was obtained when cupric chloride solutions were used as the catholyte as shown in Figure 7. When Figure 4 is compared with Figure 7, it can be seen that at low catholyte concentration, for instance 0.5 M, the limiting current densities are similar for ferric and cupric chloride.
Electrooxidation of hydrogen chloride to chlorine in a membrane equipped cell - Part I: cathode potential

Figure 5. The cathode potential as a function of current density with various concentrations of hydrochloric acid in ferric chloride solution, 50 °C.

Figure 6. The E -log a_{Cl^-} diagram for the Cu(I)/Cu(II)-Cl^-H_2O system at 20 °C.
solutions. Although when the cupric ion concentration was increased to 2.0 M, a higher limiting current density was achieved than that for the ferric chloride solution. The limiting current density for cupric chloride solution increased to 1200 A/m\(^2\), instead of 900 A/m\(^2\) as obtained for 2.0 M of ferric chloride catholyte. This may be interpreted by the higher charge of the ferric ions which could result in a larger hydration shell, making the transfer of ferric ion more difficult than those for cupric ion; an extra driving force is needed for ferric ion movement. The viscosity of ferric chloride solution is also higher than that of cupric chloride solution at the same molarity.

In contrast to the ferric chloride solution, the cupric chloride system was favoured by the presence of hydrochloric acid in the catholyte in reaching a high limiting current density as shown in Figure 8. The higher limiting current density is achieved due to the formation of cuprous chloride complex. The same concentration of sodium chloride present in the catholyte was less favourable as shown in Figure 9, probably due to the much higher chloride activity that can be reached in hydrochloric acid solution as was reported in the literature[7]. Also, the slope of the voltammogram changed with sodium chloride in the catholyte as compared to hydrochloric acid.

3.4. The influence of cathode material on the cathode potential

Due to the high price of platinum and titanium, a graphite plate which is commonly used in the electrolytic industry was tested as the cathode for the economic justification of cathode material costs. Comparing the limiting current density on graphite, shown in Figure 10, with that from the platinized titanium electrode, it is clear that the activity of graphite for the cupric reduction is much lower. Meanwhile, the cupric concentration had no significant influence on the current density when graphite was applied as the cathode. No clear limiting current density could be observed until hydrogen gas was evolved at the cathode. It appears that graphite is not suitable for the cupric reduction due to its low activity or its high overpotential to cupric reduction.
Figure 7. The cathode potential as a function of current density when various concentrations of cupric chloride are used as the catholyte, at a platinized titanium electrode, 50°C.

Figure 8. The cathode potential as a function of current density when various concentrations of hydrochloric acid are also present in the catholyte, 50°C.
Figure 9. The cathode potential as a function of current density when hydrochloric acid or sodium chloride is present in the catholyte, 50°C.

Figure 10. The cathode potential as a function of current density when using graphite as the cathode with copper chloride electrolyte at 50°C.
3.5. The influence of agitation of catholyte on the cathode potential

The reduction of ferric or cupric ions only occurs in contact with the surface of the cathode. As mentioned above, the electrode reaction was considered to be controlled by diffusion in the middle current density section. Reduction of the thickness of the diffusion layer is expected to achieve a higher limiting current density. A high flow rate of the catholyte may result in a higher limiting current density.

To minimise the thickness of diffusion layer, nitrogen gas was bubbled through the catholyte. Figure 11 shows the resulting voltammograms of the 0.5 M CuCl₂-0.1 M CuCl-1.8 M HCl system. The limiting current density increased with nitrogen sparging. When nitrogen agitation was applied, the influence of the cupric concentration on the limiting current density was much smaller as shown in Figure 12. This means that the electrode reaction was primarily kinetically controlled with gas agitation.

As previously mentioned, the limiting current in the ferric system was lower than that of the cupric system, at least without extra agitation of the catholyte, and especially for high concentrations, such as 2.0 M, as shown in Figures 4 and 7. A tremendous change occurred when nitrogen sparging was introduced into the ferric catholyte as shown in Figure 13. At a molarity of 2.0 M, the limiting current densities measured for the cupric and ferric system are similar under agitation.

For practical and cost considerations, agitating the cathode compartment with air was also carried out. When the sparging gas was shifted from nitrogen to pressurized air, the results improved as shown in Figure 13, probably due to the fact that part of the ferrous from the catholyte was reoxidised by the oxygen in the air. The same positive result would be expected to occur in the cupric system as well, because cuprous is more readily oxidised by oxygen than ferrous.
Figure 11. Voltammograms for 0.5 M CuCl₂-0.1 M CuCl-1.8 M HCl system at a platinized titanium electrode, 50°C.

Figure 12. Voltammograms for various composition of catholyte with nitrogen agitation at a platinized titanium electrode, 50°C.
Figure 14 shows that the influence of air sparging on the limiting current density of ferric reduction is more beneficial with dilute ferric chloride solutions, especially at a ferric concentration of 1.0 molarity. The limiting current density increased more than three times due to the air sparging in the catholyte. It is worthy to note that with air sparging the limiting current density for 1.0 M ferric chloride solution was slightly larger than that at the 2.0 M solution. This may be a result of the higher viscosity of the more concentrated solution. Obviously 1.0 molar ferric electrolyte can supply sufficient ferric ions to the cathode surface.

It is reasonable that nitrogen sparging had a very small effect on the limiting current density of cupric reduction when hydrochloric acid was not present in the catholyte, as shown in Figure 15. The turning point of the E -j curve appeared neither in the case without extra agitation nor with nitrogen sparging in the tested potential range. The electrode reaction was mainly kinetically controlled in both cases. This implies that hydrochloric acid was necessary for complexing.

![Graph showing cathode potential versus current density](image)

**Figure 13.** Voltammograms for 2.0 M FeCl₃-0.1 M FeCl₂-3.8 M HCl system at a platinized titanium electrode, 50°C.
Figure 14. Voltammograms for various compositions of ferric at a platinized titanium electrode catholyte with nitrogen sparging, 50°C.

Figure 15. Voltammograms for 2.0M CuCl$_2$-0.1 M CuCl system at a platinized titanium electrode, 50°C.
4. CONCLUSIONS

The following conclusions can be drawn from the experimental results for the electrolytic oxidation of HCl in a membrane equipped cell:

1) As expected, a much lower cathode potential was achieved by substituting cathodic hydrogen gas generation with cupric or ferric ion reduction.

2) A high ferric or cupric chloride concentration was favourable in obtaining a higher limiting current density, i.e. the current density at which hydrogen gas starts to evolve.

3) The presence of hydrochloric acid resulted in a higher limiting current density with the cupric, but not with ferric system. This is thought to be due to the different complexing ability of chloride to ferrous and cuprous.

4) Nitrogen or air sparging in the cathode compartment brought a much higher limiting current density, especially favoured in the case at low concentration of ferric or cupric in the catholyte.

The large limiting current density from ferric and cupric reduction enables electrolysis to be carried out at a larger current density without hydrogen evolution at the cathode, which will results in a higher production for a given volume per unit time, consequently, a low capital cost for plant construction.

5. REFERENCES

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2. Oronzio de Nora, Impianti Elettrochimici, Milano, Italy.
5. U.S. Patent 2,468,766

Chapter 9

ELECTROOXIDATION OF HYDROGEN CHLORIDE TO CHLORINE IN A MEMBRANE EQUIPPED CELL
PART II. OPERATIONAL RESULTS

1. INTRODUCTION

In the companion paper[1], the possibility of using ferric and cupric reduction as the substitute for the hydrogen gas evolution at the cathode has been discussed. A satisfactory current density and cathodic potential were achieved with these polyvalent metal ions when operating with air sparging.

In the present chapter, electrolysis of hydrogen chloride was conducted in a membrane cell with ferric or cupric reduction as the cathodic reaction. The catholyte was circulated from the cathode compartment and brought into contact with air for the reoxidation of ferrous and cuprous to ferric and cupric. Testwork on the cell voltage and the current efficiency from the ferric and cupric system are reported. The feasibility of reoxidation of ferrous and cuprous in the catholyte is discussed.

2. EXPERIMENTAL DETAILS

The reoxidation of ferrous or cuprous was carried out externally from the cathodic compartment with activated carbon particles (Norit) as a catalyst.

The electrolyses were carried out galvanostatically by using a power supply (E 015-20 Delta Electronika). The cell voltage was measured by connecting a voltmeter to the anode and the cathode.

The hydrochloric acid, cupric chloride and ferric chloride used were of chemical grade. The solutions were prepared by dissolving the salt or diluting the acid in distilled de-ionised water.
The hydrochloric acid concentration was determined by titration with standard sodium hydroxide solution using methyl red as the indicator.

The cupric ion concentration was measured by the standard iodometry. The cuprous concentration was determined by the following procedure. A sample was quickly added to a ferric ammonium sulphate solution. The amount of ferrous formed was oxidised to ferric again with 0.1 N ceric sulphate solution using Ferroin as indicator. The same method was used for the determination of ferrous concentration in the catholyte.

The chlorine concentration in the electrolyte was measured by adding KI solution and titrating iodine with 0.1 N sodium thiosulphate.

3. RESULTS AND DISCUSSIONS

3.1. Cell voltage

One of the parameters influencing the return on investment in the electrolytic industry is energy consumption, expressed in kilowatt hours per unit weight of product, \( P \), which is directly related to the cell voltage, \( E_{\text{cell}} \), and the current efficiency, \( \zeta \), as:

\[
P = \frac{k \times E_{\text{cell}}}{\zeta}
\]  

(1)

Where \( k \) is a constant specifically for a certain chemical reaction. For chlorine evolution, the value of \( k \) is 0.685 A h Kg\(^{-1}\).

When the electrolysis is carried out at high current density the cell voltage \( E_{\text{cell}} \) is given by:

\[
E_{\text{cell}} = (E^A_e + \eta_s) - (E^C_e + \eta_C) + IR_{\text{electrolyte}} + IR_{\text{membrane}} + IR_{\text{contact}}
\]  

(2)
where $E^A_e$ and $E^C_e$ are equilibrium potentials for the anodic and cathodic reaction respectively. $\eta_A$ and $\eta_C$ are respectively the overpotentials for the given anodic and cathodic reaction at a certain current density. $R_{\text{electrolyte}}$ and $R_{\text{membrane}}$ represent the electrical resistance from electrolyte and membrane respectively. $R_{\text{contact}}$ is the resistance from the outer connection circuit.

In this chapter, the contribution of the contact resistance is ignored because of its low value. The influence of the remaining three parameters on the cell voltage is described in the subsequent section.

3.1.1. The voltage drop in the electrolyte and membrane

The voltage drop over the electrolyte is related the conductivity of the solution and the distance of the electrodes. For the hydrochloric acid solution, at low HCl concentration, the conductivity increases at first with concentration; it reaches a maximum and then decreases rapidly with further increasing HCl concentration, as shown in Figure 1. As mentioned before[1], a high hydrochloric acid concentration will bring a high chloride activity in the anolyte, which is favourable for chlorine evolution. Therefore, a compromise should be made in the electrolyte concentration for the consideration of conductivity and chloride activity.

Usually, the total voltage drop over the electrolyte and membrane is obtained by subtracting the anodic potential and cathodic potential from the cell voltage, while ignoring the iR drop from the contact. In practice the voltage drop over the membrane and the electrolyte can also be measured separately by placing reference electrodes with a Lurgin tube at both sides of the membrane. Figure 2 shows that the voltage drop over the ion exchange membrane was less than 0.3 V at a current density of 2000 A/m², while the voltage drop over the electrolyte was around 0.45 V. The slope of voltage drop curve for the electrolyte is somewhat steeper than for the membrane. The voltage drop of the electrolyte is simply proportional to the distance of the anode from the cathode. In the present testwork, the electrode distance was 80 mm. The
Figure 1. The specific conductivity of hydrochloric acid solution as a function of concentration at 293 K and 323 K.

Figure 2. Voltage drop over the membrane and the electrolyte as a function of current density in a 2.0 M CuCl₂-0.1 M CuCl-3.8 M HCl system at 323 K.
voltage drop over the electrolyte could be minimised to less than 0.15 V by reducing the electrode distance to 10 mm. Another important phenomenon is that the total iR drop over the electrolyte and membrane is slightly higher when nitrogen sparging is used in the anolyte, as shown in Figure 3. This can be understood by assuming that the application of gas bubbles introduce a non-conductive phase into the electric current path in the cell. Therefore, a compromise may have to be made between a thin diffusion layer and a reasonable iR drop when sparging is used. Meanwhile, it can be seen that the iR drop in the cupric system is lower than that in the ferric system.

![Graph showing iR drop vs. Current Density](image)

Figure 3. The influence of nitrogen agitation on the iR drop over the membrane and electrolyte with a 2.0M CuCl₂-0.1 M CuCl-3.8 M HCl and a 2.0 M FeCl₃-0.1 M FeCl₂-3.8 M HCl system as catholytes.

3.1.2. Cell voltage as a function of the electrolyte composition, and the current density

Figure 4 shows that the cell voltage increases linearly as a function of current density. Similar to the iR drop, the cell voltage for the ferric system was higher than that for the cupric solution. This could be due to the higher charge number of ferric ions, which requires a higher force for ferric ion migration than for cupric ion migration.
Compared to the cell voltage in conventional hydrochloric acid electrolysis[2], the present cell voltage was much lower at a current density of 1000 A/m\(^2\), as shown in Table 1. As mentioned before, the most important factors determining the cell voltage are anodic and cathodic potentials. A lower electrode potential can be achieved not only by choosing an ideal electrode material with a low overpotential for a certain reaction, but also by enlarging the real surface area. In a platinized solid polymer electrode, the real surface area is 2000 times larger than the geometric surface area[3]. The actual current density is much lower than the geometric operating current density, therefore, a very low overpotential can be reached at this type of electrode. Meanwhile, the operation temperature can have a larger influence on electrode potential and cell voltage in the system than that shown in the Nernst equation. It has been reported that a 10 °C temperature increase results a 0.2 V cell voltage drop in the similar system[4] due to other reasons. In the present testwork, the cell temperature was only 50 °C, which is 30 to 40 °C lower than the temperature in a commercial hydrogen chloride electrolyzer. This was due to cell material limitations. Thus the cell voltage at 80 °C might become as low as 1.15 V. However, the price of electric power and heat should be taken into consideration when the cell is intended to be operated at a relatively high temperature, thus reducing the overall gain in efficiency.

Table 1. Cell voltage comparison

<table>
<thead>
<tr>
<th>cell voltage(V) at current density of 10(^3) A/m(^2)</th>
<th>conventional result 2.62 (80°C)</th>
<th>present result 2.00 (50°C)</th>
<th>expected result at 80°C 1.15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ferric system</td>
<td>Cupric system</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. The cell voltage as a function of current density when electrolysis is carried out in a 2.0M CuCl₂-0.1 M CuCl-3.8 M HCl and a 2.0 M FeCl₃-0.1 M FeCl₂-3.8 M HCl system at platinized titanium electrode.

3.2. Current efficiency

Current efficiency is another critical factor that determines the power consumption in any electrolysis process. The current efficiency is mainly determined by the number of side reactions. In the case of chlorine production, two side reactions may occur: (1) oxygen evolution; and (2) the formation of chlorate. For DSA® a high anodic overpotential for the side reactions is required, thus enabling a high current efficiency for the Cl₂ production.

Table 2 shows the solubility of chlorine in water. It can be seen that the solubility of chlorine in water decreases nearly 50% when the temperature increases from 20°C to 50°C.[5]. However, in hydrochloric acid solution the solubility of chlorine increases as the concentration of hydrochloric acid is increased and the solubility of chlorine gas in hydrochloric acid solution is slightly higher than that in water. Certain amounts of chlorine dissolved in the anolyte could also diffuse through the membrane to the catholyte and be lost in the catholyte circuit.
Table 2. Solubility data of chlorine in water[5]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (g Cl₂/100g H₂O)</td>
<td>0.9972</td>
<td>0.8495</td>
<td>0.7293</td>
<td>0.6413</td>
<td>0.5723</td>
<td>0.4590</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td>80</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Solubility (g Cl₂/100g H₂O)</td>
<td>0.3925</td>
<td>0.3295</td>
<td>0.2793</td>
<td>0.2227</td>
<td>0.1270</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Because of the water transported by protons through the cation exchange membrane, the chlorine dissolved in the anolyte certainly would leak to the catholyte. Assuming the hydration number of protons is four, the water transported by protons was 1.0 mole per hour in the present testwork at a current density of 1500 A/m². Provided all chlorine dissolved in the anolyte is transported along with water molecules, it is calculated that there would be approximately one percent leakage of chlorine to the catholyte. Meanwhile, this amount of water transport through the membrane does not cause any serious problem in the water balance of the system.

Unfortunately, when ferric reduction is used as the cathodic reaction, the ferrous ions reduced at the cathode could diffuse through to the cation exchange membrane to the anolyte and be oxidised by chlorine in the anolyte, even though the ferrous diffusion is against the direction of the electric field. When cupric reduction is used as the cathodic reaction, the situation is different from that of ferric chloride because of the complexing ability of cupric and cuprous with chloride ions. Table 3 shows the concentration distribution of different cuprous species at various chloride concentrations when the total cuprous concentration in the solution is a molality of 0.157 [6]. These data indicate that the free cuprous ion concentration in the catholyte is extremely low when the free chloride concentration has higher than 0.625 molality. No cuprous ion diffusion would be expected through a cation exchange membrane.
Table 3. Equilibrium concentration distribution of different cuprous species with various chloride concentrations[6]

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total [Cl⁻]</td>
<td>1.0</td>
</tr>
<tr>
<td>Free [Cl⁻]</td>
<td>0.625</td>
</tr>
<tr>
<td>Cuprous ions</td>
<td></td>
</tr>
<tr>
<td>[Cu⁺]</td>
<td>1.366x10⁻⁷</td>
</tr>
<tr>
<td>[CuCl₂⁻]</td>
<td>0.1065</td>
</tr>
<tr>
<td>[CuCl₃²⁻]</td>
<td>0.0401</td>
</tr>
<tr>
<td>[CuCl₄⁴⁻]</td>
<td>0.0104</td>
</tr>
<tr>
<td>[Cu(I)]Total</td>
<td>0.157</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>2.507</td>
</tr>
<tr>
<td></td>
<td>4.567x10⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>0.0384</td>
</tr>
<tr>
<td></td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>0.0606</td>
</tr>
<tr>
<td></td>
<td>0.157</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>4.457</td>
</tr>
</tbody>
</table>

Table 4 shows the current efficiency in the cupric and ferric systems respectively. They are at least 5% higher than the current efficiency in the diaphragm cell[7]. Meanwhile, the current efficiency in the cupric system is 5% higher than that in the ferric system. The current efficiency in the ferric system could be improved by operating the electrolysis at a higher current density, because the larger potential difference retards ferrous diffusion to the anolyte.

Table 4. Current efficiency under various composition of catholytes.

<table>
<thead>
<tr>
<th>Initial catholyte composition</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 M FeCl₃-0.1M FeCl₂-3.8 M HCl</td>
</tr>
<tr>
<td>Efficiency(%)</td>
<td>92-95%</td>
</tr>
</tbody>
</table>

3.3. Closing the process loop: the reoxidation of low valent metal ions in the catholyte

When ferric or cupric reductions are used as the cathodic reaction instead of hydrogen gas evolution during the electrolysis of hydrochloric acid, the low valent metal ions, such as ferrous and cuprous, which are produced at the cathode, need to be reoxidized for recirculation. In this testwork, ferrous and cuprous were reoxidised externally by oxygen.

3.3.1. Oxidation of ferrous in sulphuric acid solution

The oxidation of the ferrous ion by oxygen in aqueous sulphuric acid solution,

\[ 2 \text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \]

has been extensively investigated[8-19]. Both the reaction kinetics[8-12] as well as the effects of some physicochemical variables[13-19] have been established. It has been found that the Fe(II) oxidation rate decreased with the concentration of sulphuric acid up to 0.6 mol/l, although no effect was observed at sulphuric acid concentrations exceeding 1.0 mol/l[13]. It has also been reported that the rate of Fe(II) oxidation increases when anions that could complex Fe(III) were introduced to the reaction mixture. The effect of \( \text{H}_2\text{PO}_4^- \) and \( \text{H}_2\text{P}_2\text{O}_7^{2-} \) anions on the kinetics of ferrous oxidation has been studied by Cher and Davidson[14] as well as by King and Davidson[15], while Weiss[16] and Posner[17] have examined the effects of F- and Cl- anions respectively. All of these authors came to the conclusion that, when complexing anions were introduced, the rate of ferrous oxidation by oxygen in aqueous sulphuric acid solution was described by a first-order kinetic equation. However, the ferrous oxidation rate in a pure sulphuric acid solution follows a second-order kinetic equation.

Ferrous oxidation has also been examined under elevated oxygen pressure[18,19]. It was found that the oxidation rate of ferrous increased with oxygen partial pressure up to 2600 kPa. To increase the oxidation rate of the
ferrous ion, other methods have also been tried, including the application of bacteria, such as the Thiobacillus ferrooxidans, and mixture of oxygen and sulphur dioxide instead of only oxygen[20,21].

3.3.2. Oxidation of ferrous in hydrochloric acid solution

When the reoxidation of ferrous was carried out in the hydrochloric acid solution with charcoal as a catalyst at room temperature, the experimental results from Posner[17] can be expressed as :

\[ \frac{d[Fe^{3+}]}{dt} = k[Fe^{2+}][O_2][H^+][C] \]  \hspace{1cm} (3)

where [C] is the catalyst concentration.

The presence of the term [C] suggests that the rate is proportional to the surface area of catalyst. The acidity also had a positive influence on the ferrous oxidation rate.

![Figure 5](image)

The linear dependence of log(\%Fe^{2+} remaining) on time for various carbon catalyst concentrations at $\Sigma Fe = 0.061$ M, [HCl] = 2.0 M, $T = 289$ K, plotted by using data from Posner[17].
Figure 5 shows the ferrous concentration remaining in the solution as a function of time at various catalyst concentrations. The ferrous reoxidation was carried out as a batch experiment. With a large surface area of activated carbon as the catalyst, ferrous can be reoxidised immediately. In present electrolysis testwork, the ferrous ion produced at the cathode was about 0.215 mole per hour when the current density was 1500 A/m². With sufficient catalyst, the ferrous reoxidation is not problematic and could even be achieved by air sparging, if the carbon catalyst was present in the cathode compartment. The ferrous reoxidation rate in hydrochloric acid solution is proportional to the proton concentration as shown in Equation (3). Figure 6 shows the slope of kinetic curve as a function of hydrochloric acid concentration at constant catalyst concentration. As reported in literature, a very high proton activity can be achieved in hydrochloric acid solution[22]. Therefore, ferrous reoxidation is not the rate determining step in the whole process.

![Graph showing the relationship between reaction velocity and hydrochloric acid concentration.]

**Figure 6.** The linear relationship between the reaction velocity and hydrochloric acid concentration. $\Sigma Fe = 0.055$ M, at 289 K, plotted by using data from Posner[17].
The investigation of cuprous reoxidation has not been as intensive as that for ferrous. Only few references are available in literature[23]. Although the free cuprous concentration is extremely low, the cuprous can still be oxidised by air[17]. Air oxidation under conditions of high HCl activity may result in HCl stripping, however.

\[4\text{Cu(Cl)}_3^{2-} + 4\text{H}^+ + \text{O}_2 \rightarrow 4\text{Cu}^{2+} + 4\text{H}_2\text{O} + 12\text{Cl}^-\]

Commercial applications of this work suggest a connection with the thermal oxidation of HCl gas (the Deacon Process, using a copper chloride catalyst) where the HCl tail gas could be electrooxidized to increase overall Deacon Process efficiency. In connection with the fluid bed or spray roaster pyrohydrolysis of iron chloride solution, it allows production of chlorine instead of HCl for recycle to the process producing the iron chloride.

4. CONCLUSIONS:

From results and discussion, the following conclusion can be drawn:

(1) Electrolysis of hydrochloric acid was carried out at an attractive cell voltage with polyvalent metal ion reduction used as the cathodic reaction.

(2) The reoxidation of ferrous and cuprous was realised by air with activated carbon as the catalyst at a sufficient rate.

(3) The current efficiency in the membrane cell is much higher that that of diaphragm cell, meanwhile, the current efficiency of the cupric chloride system was higher than that from ferric chloride system.
5. REFERENCES:


Summary of the Dissertation

In hydrometallurgical processes, the regeneration of lixiviant for further treatment of the raw material is of the same importance as the recovery of metals. Preferably, the lixiviant utilized should be regenerated as its original specie, for instance the regeneration of sulphuric acid in zinc sulphate electrowinning. However, when hydrochloric acid is used as lixiviant for base metal mineral leaching, in the electrowinning stage chlorine gas instead of hydrochloric acid is produced at the anode. The regeneration of hydrochloric acid is realized by burning this chlorine with hydrogen, followed by an absorption step of the hydrogen chloride gas produced. Meanwhile, it is not economically, nor technically attractive to convert metal chloride into metal sulphate before electrowinning. The direct chloride regeneration in the form of hydrochloric acid during base metal chloride electrowinning was recognized as a “missing link” and became the first part of this dissertation.

Because the overpotentials of chlorine evolution are lower than that for oxygen at known electrode materials, it is difficult to produce oxygen directly without any chlorine evolution at the anode during base metal chloride electrowinning. Two Approaches were investigated to regenerate chloride in the form of hydrochloric acid:

In the first approach, using an ion exchange membrane electrowinning cell, water instead of chloride was oxidized at a Dimensionally Stable Anode or DSA®. In a one-membrane electrowinning cell, hydrochloric acid was able to be regenerated in the catholyte, but this resulted in an acidity increase in the catholyte and a relatively low current efficiency at the cathode. In a two-membrane cell, hydrochloric acid was regenerated in the ampholytic compartment. A relatively constant pH was maintained in the catholyte and the cathode current efficiency was satisfied. The amount of chloride leaking from the ampholyte to the anolyte was minimized either by using a cation ion exchange membrane with better anion reject characteristics or by using multi-layer membranes. It was another option to remove the trace of chloride in the anolyte by silver chloride precipitation.
In the second approach, also using an ion exchange membrane cell setup, but hydrogen was oxidized to protons at a Hydrogen Diffusion Anode, or HDA, which resulted in a low cell voltage for the electrowinning. Hydrochloric acid was regenerated in the anolyte. Performance deterioration of the HDA has not been observed even in 3.0 M HCl solution.

The subject of second part of this dissertation, the production of chlorine by hydrogen chloride electrolysis, appears not to have a direct connection with the first part, the production of metals. It even seems superfluous to the first part. Excess HCl is a problem, however, not only in organic chlorination processes, but also in the minerals processing industry. In particular the processing of titaniferrous ores requires dry chlorination to yield TiO₂ pigments and to recover chlorine. The organizations which produce chlorine and excess HCl can not utilize each others by-products due to transportation hazards and costs. A process to electro-oxidize wet HCl would meet a technological, environmental and economic need.

In the second part, the possibility to electro-oxidize hydrogen chloride to chlorine at a low cell voltage has been investigated. With DSA® already available as the anode, the anodic potential can hardly be improved. Attention was therefore mainly focused on the reduction of the cathode potential. The adoption of ferric or cupric reduction instead of proton reduction as the cathodic reaction in membrane electrolyzer gave promising results, especially when air sparging was used in the cathode compartment. A high hydrochloric acid concentration in the catholyte was found to be favorable to obtain a high current density for cupric reduction. Ferrous or cuprous ions produced at the cathode can be re-oxidized economically with oxygen from air externally or even in the cathode compartment of the cell.
Samenvatting


De overpotentiaal voor de vorming van chloorn aan alle bekende anodematerialen is lager dan die voor de vorming van zuurstof. Het is daardoor vrijwel onmogelijk, bij directe electrowinning in chloride bevattende oplossingen, aan de anode zuurstof te produceren zonder gelijktijdige chloornvorming.

Er zijn twee celtypes onderzocht om te trachten toch regeneratie tot zoutzuur te realiseren. Bij het eerste celtype wordt gebruik wordt gemaakt van een cel waar de katholiet van de anoliet gescheiden wordt door een ionselectief membraan. Nu wordt water aan de anode geoxideerd in plaats van van chlorine-ioniën. Er wordt een "Dimensionally Stable" anode (DSA®) gebruikt. Weliswaar wordt er nu zoutzuur in het katholiet gevormd maar de daardoor veroorzaakte toename van de zuurconcentratie is oorzaak van een relatief geringe stroomefficiëntie bij de electrowinning.

In het tweede onderzochte celtype wordt gebruik gemaakt van een cel waarin zich twee membranen bevinden. In deze cel wordt het zoutzuur geregenerereerd in het ampholiet, de vloeistof in het compartiment tussen de beide membranen. De pH in het katholiet blijft veel constanter en de stroomefficiëntie voldoet aan de eisen. De kleine hoeveelheid chloride die uit de ampholiet naar de anoliet lekt kan geminimaliseerd
worden door keuze van een kationselectief membraan met minimaal aniontransport of door een kationselectief membraan dat uit meerdere laagjes membraan is opgebouwd. Een andere mogelijkheid om het effect van chloride lekkage naar het anoliet tegen te gaan, vormt het neerslaan van het chloride als zilverchloride.

Een geheel andere oplossing voor een anodesysteem waarbij zoutzuur wordt geregenereerd is de waterstofdiffusie anode (HDA). Tussen de kathode en de HDA bevindt zich een ionselectief membraan. Aan de HDA wordt waterstof geoxideerd tot protonen. Zoutzuur wordt dus direct gevormd in het anoliet. Het gebruik van deze HDA resulteert in een gunstige lage celspanning voor de electrowinning. Het gebruik van de toegepaste HDA verloopt zonder problemen zelfs in 4.0 M HCl oplossing.

Het tweede deel van dit proefschrift, het onderzoek naar de productie van chloor door electrolyse van zoutzuur, heeft schijnbaar weinig te maken met het eerste deel van dit proefschrift: de productie van metalen. Het komt mogelijk zelfs overbodig over. Een overschot aan HCl is echter een probleem niet alleen bij organisch chemische chloreringsprocessen maar ook in de ertsverwerkende industrie. De verwerking van titaniumertsen tot TiO₂ pigmenten vereist droge chlorering van titaniumertsen gevolgd door regeneratie van chloor. De bedrijven die chloor en zoutzuur als bijproducten produceren kunnen elkaars bijproducten niet gebruiken vanwege transportgevaren en kosten. Daarom is een proces om electrochemisch zoutzuur te oxideren tot chloor technologisch, milieutechnisch en economisch van belang.

In dit tweede deel van het proefschrift wordt onderzocht hoe de electrochemische omzetting van zoutzuur tot chloor met behulp van een cel met een zo laag mogelijke celspanning kan worden gerealiseerd. De anodepotentiaal waarmee aan een DSA® chloor kan worden gevormd is nauwelijks meer voor verbetering vatbaar. Daarom is voornamelijk aandacht besteed aan het optimaal maken van de kathodepotentiaal. In plaats van de gebruikelijke reductie van protonen tot waterstof als kathodereactie is gebruik gemaakt van de reductie van koper(II) tot koper(I) of van Fe(III) tot Fe(II) als kathode reactie. Het geeft veelbelovende resultaten speciaal als de katholiet belicht wordt. Een hoge zoutzuurconcentratie in het katholiet is een vereiste om een hoge stroomdichtheid te realiseren aan de kathode in het geval van de reductie van Cu(II) tot Cu(I). De aan de kathode gevormde Fe(II)-ionen of Cu(I)-ionen kunnen eenvoudig geoxideerd worden met zuurstof of lucht in of buiten het kathodecompartiment.
Acknowledgments

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CURRICULUM VITAE

Lun-Zhi Liao

Personal Information

Date of birth: 24 May 1962
Place of birth: Jiangxi Province, P. R. China
Sex: male

Education & Professional Training

Advanced Courses on Membrane Technology, Stuttgart, Germany, March 1995.
M.Sc. in Chemistry, Yunnan University, P.R. China, 1986.
B.Sc. in Chemistry, Jian Teachers College, P.R. China, 1982.

Employment

April 1997--- Jan. 1993
"Assistent in Opleiding" (AI0) at the Faculty of Applied Earth Sciences,
Delft University of Technology.

Research assistant in the Laboratory of Process and Equipment,
Faculty of Chemical Engineering, Delft University of Technology.

Nov. 1991--- Aug. 1986
Lecturer in the Department of Chemistry, Yunnan Normal University,
Kunming, P.R. China.
Concurrent position as a part-time engineer at Yunnan Patent Tech.
Corp., Kunming, China.

Chemistry teacher in Taihe No. 2 High School in Jiangxi province, P.R.
China