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HYDROGEN EVOLUTION IN KF.2HF

by

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A Doctoral Thesis submitted in partial fulfilment of the requirement for the award of Doctor of Philosophy of the Loughborough University of Technology.

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SUMMARY

This thesis describes an electrochemical investigation of the processes occurring at the hydrogen evolving cathode during the industrial production of fluorine in molten KF.2HF. A 1A laboratory cell, designed for the purposes of the project, is described. Observations of the operation of this cell are reported. A comparison of a range of electrode materials is given, both with regard to electrochemical overvoltage and the bubbling releasing characteristics, for which photographic evidence is presented. In addition, measurements of the ohmic potential drop, caused by the presence of bubbles, were made for different bubble types. Included in the above is a description of any effects of metallic impurities present in the melt both on overvoltage and bubble release. A mechanistic study of hydrogen evolution on platinum is described and compared with the reaction at a mild steel electrode. A preliminary investigation into the use of parallel strand expanded metal electrodes was made and further photographic evidence presented.

The work described in this thesis has not been submitted, in full or in part, to this or any other institution for a higher degree.

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CHAPTER 1

INTRODUCTION

In the 1770's William Scheele prepared crude hydrofluoric acid by heating fluorospar with sulphuric acid and observed that the vapours produced etched gas. It was, however, Sir Humphrey Davy who recognised the presence of a new element in the compound and described the discovery in a paper presented to the Royal Society of London on 8th July, 1813. The name fluorine was suggested by Ampère and the element was described as "a peculiar substance, possessed of strong attractions for metallic bodies and hydrogen, and which combined with certain inflammable bodies forms a peculiar acid, which in consequence of its strong affinities and high decomposing agencies, it will be very difficult to examine in a pure form".

It is only within the last fifty years that it has been possible to produce fluorine on an industrial scale. The key to the process was the ready availability of anhydrous hydrogen fluoride (AHF) in commercial quantities. Before this time (1931 in America, 1941 in England) the use of fluorine compounds was limited to calcium fluoride as flux in metallurgical processes and aqueous hydrofluoric acid in a variety of applications. The need to produce AHF arose because it was a raw material in the production of non-toxic, noninflammable refrigerants [1,2].

As with many other chemical products, the preparation of fluorine and its compounds developed at a remarkable rate during the Second World War, in Germany, England and America. In the former case it was for the manufacture of chlorine trifluoride for use as an incendiary device and in the latter two for the manufacture of uranium hexafluoride. At the present time one of the main commercial outlets of fluorine remains the atomic energy industry where it is essential for the reaction:

 $UF_4 + F_2 \rightarrow UF_6 \tag{1.1}$

The hexafluoride is fed to the diffusional separation plants for the separation of 235 U in natural uranium. Other uses are for fluorine-

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rich oxidisers in rocketry and for sulphur hexafluoride which is used as a gaseous dielectric in electrical equipment.

The work described in this thesis concerns the present-day system for the production of fluorine, which includes a molten KF.2HF electrolyte, porous carbon anode and mild steel cathode. It is the reaction at the latter hydrogen evolving electrode which has been investigated. The design of a simple 1A cell is described, upon which the initial observations of the processes occurring during operation of the cell were made. This is followed by a comparison of various metals as cathode material, which also gives some insight into the effects of any metallic impurities in the melt. A mechanistic study of hydrogen evolution on platinum is described and compared with the reaction at a mild steel electrode.

The quantification of ohmic potential drop caused by the presence of bubbles in the interelectrode gap is described. This also includes the effect of the deposition of impurities on bubble characteristics. The work is supported by photographic evidence of the variation of bubble size and contact angle with time, electrode material and current density. This section is of particular interest due to the previous scarcity of visual information.

The impurity content and variability of industrial electrolyte has made it difficult to ascribe definitive numerical constants to the electrochemical system. In order to obtain some quantitative information "pure" electrolyte was prepared. This proved to be both a time consuming and arduous task. However, a number of small batches were produced allowing linear sweep voltammetric studies at platinum electrodes to be undertaken. This data complements the industrially relevant information obtained from commercially available electrolyte.

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CHAPTER 2

HISTORICAL BACKGROUND

2.1 Laboratory Cells

2.1.1 Low Temperature Cells

Elemental fluorine itself was isolated by Henri Moissan in 1886 [3]. His method involved the electrolysis of KF.12HF contained in a platinum U-tube with anode and cathode also of platinum. The whole cell was maintained below room temperature to avoid excessive loss of HF. However, the rate of corrosion of the cell was high, 5-6 g of platinum being consumed for every gram of fluorine produced. The use of a copper cell reduced the corrosion problem [4] and Poulenc and Meslans [5] proposed the use of a cylindrical cell body, a perforated diaphragm and an internally cooled anode. However, it was not reported that the cell functioned successfully.

At this stage progress was hampered by the dangers of handling hydrogen fluoride and by the lack of a convenient supply of anhydrous hydrogen fluoride (AHF). In the period 1886 to 1919 only six papers concerned with elemental fluorine were produced and in the next 20 years only twenty-five papers and nine patents appeared. Between 1936 and 1942 ICI investigated the use of a low temperature cell with an electrolyte of KF-8HF, operating at room temperature [6]. However, corrosion problems caused the project to be abandoned.

2.1.2 High Temperature Cells

Argo et al [7] developed a cell using anhydrous potassium bifluoride as electrolyte, operating at 250°C. The cell body was of copper and acted as the cathode, whilst the anode was of Acheson carbon. This design avoided the need for AHF and platinum equipment. However, the composition of the electrolyte had to be maintained within narrow limits as the melting point of the electrolyte rises sharply as hydrogen fluoride is depleted. Furthermore, anode polarisation caused severe problems.

Forty patents and papers appeared in the period 1919 to 1944,

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describing various high temperature cells. These were mainly of a diaphragm type although 'V' or 'U'-shaped cells were also proposed. Attempts were made to isolate the diaphragm to prevent its corrosion. Other designs described graphite cells, employed in a bid to overcome corrosion but these proved fragile. Air cooled electrodes entering through the base of the cell were proposed. Bodenstein et al [8] used an Elektron alloy (98% Mg, 2% Mn) tank with a louvred Elektron diaphragm, silver cathode and graphite anode. Some of the many features described were later used in the design of industrial scale cells.

A practical laboratory scale cell was described by Simons [9] and this was subsequently developed into a 30A cell using three graphite rods as anodes.

The work undertaken on high temperature cells confirmed that copper, magnesium and silver were useful construction materials and that graphite was the most successful anode material. The important characteristics of these cells are summarised below.

(1) The product F_2 contained 5-15% volume of HF which was removed by contact with NaF.

(2) The water content of the electrolyte had to be minimised to reduce the occurrence of polarisation.

(3) A hard glassy layer of carbon monofluoride $(CF)_n$ formed on the anode leading to a poor yield and erratic operation.

(4) The electrolyte was regenerated in a separate vessel.

(5) The graphite anodes were gradually corroded to produce CF_4 , which increased contamination of the fluorine.

2.1.3 Medium Temperature Cells

A cell of this type was developed, by Lebeau and Damiens [10] in 1926, which used an electrolyte of KF.3HF (m.pt. 66°C). CF_4 contamination of the fluorine was eliminated by the use of a nickel anode. The copper tank acted as the cathode and the cell also had a copper diaphragm. No polarisation problems were observed but the anode suffered from corrosion and had a low current efficiency. The electrolyte was regenerated in situ but the high vapour pressure of HF led to considerable contamination of the fluorine. A similar cell

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described by Henne [11] used graphite electrodes and gave an improved current efficiency.

A major contribution to the subsequent development of fluorine production was the determination of the phase diagram for the potassium fluoride/hydrogen fluoride system by Cady in 1939 [12], (Figure 2.1). This led to the development of a cell with an electrolyte composition of KF.2.2.HF, operating at 75°C. The vapour pressure above the melt was very much lower than for the KF.3HF system and nickel or nongraphitic anodes were used. Later the electrolyte composition was modified to KF.2HF and the cell had a perforated diaphragm. Preelectrolysis of the KF.2HF with graphite electrodes removed water and other impurities and HF was then added. The advantages of this type of cell are summarised as follows:

(1) Regeneration of the electrolyte took place in situ.

(2) The vapour pressure of the electrolyte was low.

(3) The composition of the electrolyte could vary over a fairly wide range with only small variations in the operating temperature.

(4) Corrosion of cell materials was reduced and steel could be used in place of monel for the cell body. Furthermore, if pre-electrolysis was performed no anode surface film was formed.

2.2 Industrial Scale Cells

During the Second World War the requirements for fluorine increased for the reasons stated previously. As a result development of the cells was somewhat curtailed because of the immediate need to go into production.

While all three types of cell, low, medium and high temperature, were investigated, the low temperature process received the least attention owing to its greater difficulties of operation. Experiments were conducted by Du Pont [13], the Harshaw Chemical Company [14] and I.C.I. [6, 15] using electrolyte of KF.8-10HF at room temperature. However, the corrosion problems and low current efficiency caused the projects to be abandoned.

2.2.1 High Temperature Cells

The advantage of this type of cell was that graphite electrodes offer the possibility of high current densities. This allows a more

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Figure 2.1 Melting point versus composition diagram for KF/HF system

compact cell design, lower operating voltages and no severe polarisation problems. However, increased corrosion rates and the necessity for accurate control of the electrolyte composition are distinct disadvantages.

A 2kA German cell, using Elektron alloy as the major material of construction with graphite and silver electrodes was operated at Leverkusen [16]. Corrosion problems were overcome by the continuous addition of HF, also ensuring a constant electrolyte composition and hence, operating temperature. An American cell, with a graphite anode and using monel as the cathode and most other components, failed due to excessive corrosion problems [17]. Both cells had a solid skirt dipping into the electrolyte to keep the fluorine and hydrogen products separate. In the case of the German cell, the expense of using silver cathodes was accepted because of its resistance to corrosion and its good recovery rate from the electrolyte.

2.2.2 Medium Temperature Cells

American studies [18, 19, 20] determined the medium temperature cell to be the most practical system for producing fluorine. Initially, nickel anodes were used and the corrosion of these was a problem. Ungraphitised carbon was later used and is employed in modern cells.

A report by Ring and Royston [21] summarises the operating characteristics of the main industrial cells from 1940 to the I.C.I. cells of 1970. The main features are monel and steel tanks, carbon anodes and steel cathodes. A range of carbons are used including National Carbon Co. Type GA, YBD, YAA and Union Carbide CISA and SERS.

In Britain fluorine production started in 1948, with the first of six cells of the medium temperature type being commissioned at the Rocksavage Works of I.C.I. These cells were of a nominal capacity of 1 kA and were chiefly used to produce fluorine for the initiation of the British Atomic Energy programme. In 1952 the plant was uprated to twelve cells of nominal 1.4 kA capacity. Further developments were in 1955, when there were sixteen cells nominal 1.4 kA capacity. These were uprated to 2.2 kA in 1957 and, finally, in 1959 fourteen 5.0 kA capacity cells were installed. Their operating characteristics are shown in Table 2.1. All the product fluorine was converted to chlorine trifluoride which was almost all consumed by the UKAEA. Since 1968 the UKAEA (latterly BNFL) have produced their own fluorine requirements using a system based on cells obtained from I.C.I.

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TABLE 2.1 Operating Characteristics of I.C.I. Rocksavage Cells (1)

[1] A. Martin and M. Ma Martin and M. Martin a Martin and M. Martin and M Martin and M. Martin and M Martin and M. Martin and Martin and Ma	
Normal current capacity	5 kA
Maximum current capacity	6.5 kA
Fluorine output (Normal)	3.3 kg/h
Current efficiency	93%
Voltage at 5 kA	10 V
Anode current density	1.8 kAm ⁻²
Cathode current density	0.36 kAm^{-2}
Electrolyte Temperature	80-85°C
HF Content of electrolyte	40-41.5 wt %
Electrolyte purity and preliminary treatment	Purity not critical, cell is started at low load to remove water
HF feed purity	Purity not critical
Life of cell body	>84.5 x 10 ⁷ Ah
Life of skirt	17.6×10^7 Ah
Life of anodes	66 x 10 ⁶ Ah
Cell service life	44 x 10 ⁶ Ah
Polarisation frequency	No polarisation has ever occurred
HF in fluorine	6 Vol %
HF in hydrogen	4 Vol %
Cooling water temperature Inlet/Outlet	.65/67°C
Cell body, cover, anode support	Steel
Skirt	Monel
Anode	High permeability carbon
Internal dimensions of cell body 1 x w x h	3020 x 710 x 560 mm
Electrolyte capacity	1730 kg

Electrolyte capacity Number of anode blocks Size of anode blocks Cathode

24 (12 anode assemblies) 343 x 279 x 69.9 mm Steel coils

2.3 Operating Characteristics

Industrial fluorine cells operate at a cell voltage of 10-11 V. The equilibrium decomposition voltage, ΔE , for the process:

$$HF(1) \rightarrow \frac{1}{2}F_2(g) + \frac{1}{2}H_2(g)$$
 (2.1)

has been calculated for the electrolyte KF.2HF at 85°C to be 2.92 V * [22]. Similarly for the electrolyte KF.HF at 250°C, $\Delta E = 3.01$ V. Both these values differ considerably from experimentally determined decomposition voltages [23, 24] but there is some doubt as to whether the potential determining couples were HF-F₂ and HF-H₂. It is likely that a deposit of carbon monofluoride also influenced the anode potential. However, these papers outlined the reaction steps for fluorine evolution as:

 $(HF_2)_e + C \rightarrow HF + C \dots F + e$ (2.2)

$$C...F + C...F \rightarrow C + F_2$$

$$C...F + F \rightarrow C + F_2 + e$$

$$(2.3)$$

In addition to the decomposition voltage there is a considerable anodic overvoltage of 3V. A number of papers concerned with fluorine producing systems concentrate on the investigation of an insulating layer of solid carbon-fluorine compounds [25, 26]. The stoichiometric ratio has been estimated to be 1:1. The formation of carbon fluoride is considered responsible for the high anodic over-voltage and contributes to the disintegration of the anode. Many papers supporting this view have been published by Watanabe and co-writers [27, 28, 29]. In addition the fluoride layer is considered to decrease the wettability of the anode which is correlated with incidence of the anode effect. In general metal electrodes have good wettability and the anode effect does not occur [30, 31, 32]. Indeed the addition of metal ions to a melt is considered to aid wettability and prevent anode effect.

With these aspects in mind two research contracts between British Nuclear Fuels plc. and Newcastle University have previously been completed, in addition to in-house studies at BNF plc. The use

All electrolytes used in the production of fluorine may be regarded as solutions of potassium fluoride in anhydrous hydrogen fluoride.

of high efficiency, modified carbon anodes is seen as the likeliest way of lowering the anode overvoltage.

At 1V the cathode overvoltage has a smaller contribution to the cell working voltage. Consequently far less attention has been directed towards the hydrogen evolution reaction. Only two papers related to the subject have been found, concerning hydrogen evolution at platinum electrodes in KF.HF [33, 34]. The first paper investigated the effects of water on the reaction and gave two possible routes of hydrogen evolution

 e^{-} + HF $\rightarrow \frac{1}{2}$ H₂ + F⁻ (2.5)

 $e^{-} + H_30^{+} \rightarrow \frac{i}{2}H_2 + H_20$ (2.6)

The second paper detailed the effects of different degrees of purity of the electrolyte on the hydrogen evolution reaction and presented Tafel data which showed α to be 0.75. Another interesting observation was the presence, in some circumstances, of a voltage plateau on interruption of current.

The largest contribution to the cell operating voltage is from the electrolyte ohmic resistance of about 4V. This can be reduced by decreasing the interelectrode gap, provided that the product gases do not mix and thus reduce the yield. It is, therefore, desirable to remove gas bubbles from the interelectrode gap for two reasons. Directing the gas to the rear of the electrode prevents mixing. In addition, the void space in the electrolyte, caused by bubbles, is of very high resistance and adds greatly to the electrolyte resistivity. Another aspect is the obscuring of the electrode surface by attached bubbles which increase the effective current density on unobscured areas and causes constriction of the current distribution. One other means of decreasing overvoltage is the use of high surface area electrodes. In practice, the anode is already of high surface area. Fluorine passes upwards through its pores and is not liberated into the solution. It has been observed that at the commencement of cell operation the contact angle at the steel cathode approximates to zero, the hydrogen bubbles are spherical, relatively small and are freely evolved from the cathode [2]. These bubbles do not spread far through the electrolyte in a horizontal direction. Rudge stated that when using a cathode 12 in. deep, 95% of the hydrogen bubbles did not spreade more than 0.75 in. horizontally from the cathode face. After

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a period of operation, the bubble size increases, indicating a small, progressive increase in contact angle.

In the present study the areas of the KF.2HF system covered have been those which have received little or no attention in the past in particular the electrochemistry of the hydrogen evolution reaction, the nature of the gas liberation and the quantification of the resulting ohmic drop.

CHAPTER 3

THEORETICAL PRINCIPLES

3.1 Charge Transfer

When considering the general electrode process

$$0 + ne \stackrel{k_{f}}{\stackrel{\leftarrow}{\atop}} R \qquad (3.1)$$

$$k_{b}$$

(where k_f and k_b are the rate constants for the forward and backward reactions respectively), the Nernst equation which characterises the equilibrium is

$$E' = E^{\Theta} + \frac{RT}{nF} = \frac{\ln C_0^{\sigma}}{C_R^{\sigma}}$$
(3.2)

(where C_0^{σ} and C_R^{σ} represent the surface concentrations of the oxidised and reduced species respectively, E'is the equilibrium or reversible potential and E^{σ} is the standard electrode potential of the O/R couple). If no current has been passed, the surface concentrations are equal to those in the bulk solution and

$$E' = E^{\Theta} + \frac{RT}{nF} \quad \ln \quad \frac{C_0^{\infty}}{C_R^{\infty}}$$
(3.3)

At the reversible potential of the system the net rate of reaction, and hence net current, is zero. Therefore:

$$\mathbf{i}_{o} = \mathbf{i}_{f} = \mathbf{i}_{b} \tag{3.4}$$

 i_0 being known as the exchange current density. This parameter is an important kinetic characteristic of the electron transfer process.

The Nernst equation is based solely on thermodynamic principles and the electrode kinetics must be considered in addition. The rates of reaction of 0 and R are:

Rate of Reduction of
$$0 = k_f C_0^{\sigma}$$
 (3.5)

and

Rate of Oxidation of
$$R = k_b C_R^{\sigma}$$
 (3.6)

Therefore, the reduction and oxidation currents are:

$$i_{f} = n F k_{f} C_{0}^{\sigma}$$
(3.7)

and

$$i_b = n F k_b C_R^{\sigma}$$
(3.8)

where n and F have their usual significance. Consequently the net current, i, is given by

 $\mathbf{i} = \begin{vmatrix} \mathbf{i}_{\mathbf{f}} \end{vmatrix} - \begin{vmatrix} \mathbf{i}_{\mathbf{b}} \end{vmatrix} \tag{3.9}$

In a heterogeneous redox reaction the kinetic behaviour of any species will be strongly influenced by the interfacial potential difference. We must, therefore, consider its effect.

If it is assumed that the rate constants ${\bf k}_{\rm f}$ and ${\bf k}_{\rm b}$ follow the Arrhenius equation, it can be deduced that

$$k_{f} = A_{f} \exp \left(-\frac{\Delta \overline{G}_{f}^{\dagger}}{RT}\right)$$
 (3.10)

and

$$k_{b} = A_{b} \exp \left(-\frac{\Delta \overline{G}_{b}^{\dagger}}{RT}\right)$$
 (3.11)

where A_f and A_b are pre-exponential constants and $\Delta \overline{G}_f^{\dagger}$ and $\Delta \overline{G}_b^{\dagger}$ are the electrochemical activation free energies for the forward and backward reactions respectively. Consequently they can be separated into chemical and electrical components, thus:

$$\Delta \overline{G}_{f}^{\dagger} = \Delta G_{f}^{\dagger} + (\Delta G_{f}^{\dagger})_{e} \qquad (3.12)$$
$$\Delta \overline{G}_{b}^{\dagger} = \Delta G_{b}^{\dagger} + (\Delta G_{b}^{\dagger})_{e} \qquad (3.13)$$

where the subscript "e" denotes an electrical energy. This is illustrated in Figure (3.1).

It is assumed that the chemical components ΔG_f^{\ddagger} and ΔG_b^{\ddagger} are independent of potential and hence the effects of potential apply only to the electrical components. The total electrical energy, -nFE, is divided between the forward and reverse reactions. This fixed fraction is represented by the transfer coefficient, α , which is in the range $0 < \alpha < 1$, but is often close to 0.5.

Therefore, in the polarised state:

$$(\Delta G_{f}^{\dagger})_{e} = \alpha (\Delta G^{\theta})_{e} \qquad (3.14)$$

and

$$\left(\Delta G_{b}^{\dagger}\right)_{e} = -(1 - \alpha)\left(\Delta G^{\theta}\right)_{e} \qquad (3.15)$$

or

$$(\Delta G_{f}^{\dagger})_{e} = -\alpha n FE \qquad (3.16)$$

and

$$(\Delta G_{b}^{\dagger})_{e} = (1 - \alpha) n FE$$
 (3.17)

Substituting (3.16) and (3.17) into (3.10) and (3.11) gives:

$$k_{f} = A_{f} \exp \left(\frac{-\Delta G_{f}}{RT}\right) \exp \left(\frac{-\alpha n F E}{RT}\right)$$
 (3.18)

and

$$k_{b} = A_{b} \exp \left(-\Delta G_{b}^{\frac{1}{2}}\right) \exp \left(\frac{(1-\alpha)nFE}{RT}\right)$$
 (3.19)

If the potential independent parts are now represented by $k_{\rm f}^{~0}$ and $k_{\rm b}^{~0}$ we obtain

$$k_{f} = k_{f}^{0} \exp\left(-\frac{\alpha n F E}{RT}\right)$$
 (3.20)

and

$$k_{b} = k_{b}^{0} \exp\left(\frac{(1-\alpha)nFE}{RT}\right)$$
(3.21)



Figure 3.1 Free energy surfaces showing the electrochemical free energy, \overline{G}^{θ} , split into its components of chemical free energy, G^{θ} , and electrical energy, $(G^{\theta})_{e}$.

These equations can now be substituted into equation (3.9) to give:

$$i = nF \{ k_f^0 C_0^\sigma \exp\left(\frac{-\alpha nFE}{RT}\right) - k_b^0 C_R^\sigma \exp\left(\frac{(1-\alpha)nFE}{RT}\right) \} \quad (3.22)$$

At the reversible potential, E_{rev} , of the system the net rate of reaction and hence net current is zero. Therefore:

$$i_0 = i_f = i_b$$

and

$$i_{o} = nF k_{f}^{0} C_{o}^{\sigma} exp \left(\frac{-\alpha nFE_{rev}}{RT}\right) = nF k_{b}^{0} C_{b}^{\sigma} exp \left(\frac{(1-\alpha)nFE_{rev}}{RT}\right) (3.23)$$

Introducing the overpotential, $\eta = E - E_{rev}$, we can obtain:

$$i = i_0 \left\{ \exp\left(\frac{-\alpha nF\eta}{RT}\right) - \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) \right\}$$
 (3.24)

This is the Butler-Volmer equation and applies when a solution is well stirred or the currents are kept so low that the surface concentrations do not differ appreciably from the bulk values.

Equation (3.24) can be simplified by considering the behaviour in three defined cases.

(a) For an electrode at a very low overpotential ($\eta < approximately$ 0.02 V) the exponential e^{X} may be expanded using just the first two terms of the series, $e^{X} = 1 + x$. Then:

$$i = i_0 (1 + (-\alpha n\eta F/RT)) - i_0 (1 + ((1-\alpha)n\eta F/RT))$$
 (3.25)

Hence:

$$i = \frac{i_o(-nnF)}{RT}$$
(3.26)

which shows that net current becomes a linear function of overpotential.

(b) At large values of n one of the two terms in (3.24) becomes negligible, as the rate of the reverse reaction becomes very low. At large negative overpotentials (3.24) becomes:

$$i = i_{o} \exp \left(-\frac{\alpha n n F}{RT}\right)$$
 (3.27)

or

$$\eta = \frac{RT}{\alpha nF} \ln i_{o} - \frac{RT}{\alpha nF} \ln i \qquad (3.28)$$

and

$$\ln i = \ln i_0 - \frac{\alpha n \eta F}{RT}$$
(3.29)

which may be written as:

$$\eta = a + b \ln i \qquad (3.30)$$

as predicted by Tafel. A plot of log i vs η is linear, the Tafel constants being as follows:

$$a = \log i_{0}$$
 (Intercept) (3.31)

$$b = \frac{-\alpha nF}{2.3 RT}$$
 (Slope) (3.32)

for the cathodic branch and

$$b = \frac{(1 - \alpha)nF}{2.3 RT}$$
(3.33)

for the anodic branch (see Figure 3.2).

3.2 <u>Mass Transport Processes</u> The electrode process:

$$0 + ne \xrightarrow{k_{f}} R \qquad (3.1)$$

$$k_{b}$$

can be considered to involve the following three steps:

$$0_{\text{bulk}} \rightarrow 0_{\text{electrode}}$$
 (3.34)



Figure 3.2 Experimental determination of the kinetic constants, I_0 and α , using the Tafel equation. Deviations from linearity occur at low n, as the limiting form of the equation is no longer valid [45].

0 + ne \rightarrow R electrode	(3.35)
------------------------------------	--------

 $R_{electrode} \rightarrow R_{bulk}$ (3.36)

The overall electrode process may be totally or partially controlled by mass transfer. In the case where (3.34) or (3.36) are the slowest steps then the reaction is mass transfer controlled. If (3.35) is the slowest step, the rate of electron transfer is limiting. A third possibility exists where a chemical transformation is limiting where none of the three processes is as slow as this transformation.

Three modes of mass transport may operate in an electrolyte, which are as follows:

(1) Migration

A charged particle in an electric field will have certain forces acting on it. However, in the presence of a large excess of supporting electrolyte the migration of the electroactive material is minimised.

(2) Convection

Natural or free convection develops spontaneously in a solution undergoing electrolysis. It arises from the density differences near the electrode and may have thermal and mechanical disturbance contributions. Forced convection can arise from stirring the electrolyte, rotating the electrode and from bubbling gas near the electrode.

(3) Diffusion

Immediately electrolysis starts concentration differences develop which may result in diffusion of the electroactive species. Consequently diffusion occurs in every electrode reaction to a greater or lesser extent. The linear diffusion of a reacting species to a planar electrode in a static solution, assuming there is no migration or convection, can be represented by:

$$\frac{dN}{dt} = D_0 A \frac{\partial C_0}{\partial x}$$
(3.37)

i.e. this represents the number of moles, N, of a substance diffusing across a cross-sectional area, A (cm^2) in time ∂t , which is proportional to the concentration gradient of the diffusing species. D₀ is the number of moles per second crossing unit area

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under unit concentration gradient, i.e. the diffusion coefficient. Equation (3.37) is a representation of Fick's First Law.

3.3 Molten Salt Electrolytes

Molten salt electrolytes are utilized in a variety of industrial processes, particularly in metal extraction. Other uses include hightemperature molten salt battery and fuel cell electrolytes. In general, melts have good thermal stability, good electrochemical stability, high heat capacity, good heat transfer properties, rapid chemical and electrochemical reaction rates, high electrolytic conductivity rates and good solvent properties [35]. Very often an apparent "irreversibility" in cathodic reactions arises from a slow coupled chemical process rather than slow charge transfer.

Early research consisted of investigations of phase diagrams and measurements of melting points and heats of fusion of single component salts. Molten salts have many microscopic and macroscopic physicochemical properties in common with other liquids [36]. At the simplest level they are described as liquids composed of positive and negative ions that interact mainly via the strong long-range Coulomb potential. However, evidence tends to show that molten salts show individual or group peculiarities which complicate the understanding of their morphology.

Information on the structure of single-component molten salts has been deduced directly from spectroscopic scattering experiments. Two well established conclusions have been drawn:

(1) anions in the melt are surrounded by cations and vice versa;

(2) the anion-cation distances in the melt are shorter than those in the corresponding crystal.

Furthermore, for alkali chlorides it appears that the co-ordination numbers in the melt appear to be remarkably close to those in the solid. At temperatures close to their melting points the timeaverage structures of simple molten salts resemble the well-defined arrays of their parent crystals [35]. However, melting causes reorganization of the constituent atoms into simple and complex ions, with the creation of space between these groups.

The approach to the study of the properties of molten salts mixtures has consisted of a systematic investigation of the properties

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of the mixtures, including thermodynamic quantities and spectroscopic properties. Within these studies, five categories of molten salt have been recognised.

- (i) Equally charge-symmetrical binary systems with a common ion, e.g. NaCl-NaBr.
- (ii) Unequally charge-symmetrical binary systems with a common ion, e.g. MgCl₂-CaCl₂.
- (iii) Charge-unsymmetrical binary systems with a common ion,e.g. NaNO₃-Pb(NO₃)₂.
- (iv) Reciprocal binary mixtures in which two salts have no common ion are mixed to form a melt with four ions. Depending on the ion charges, reciprocal mixtures can be symmetrical or unsymmetrical, e.g. KC1-NaBr, CaCO₃-Na₂SO₄.
- (v) Ternary (or higher) systems in which three (or more) salts are mixed in any of the above combinations.

When in a molten mixture of salts the ingredients interact to form complex compounds, clusters and ion pairs [37]. The interactions are an example of the general process of solvation. In studies with molten salts, the solvent supplies the ligands for the complex compounds. In aqueous systems not only the complex compound but the ligands themselves are solutes, usually dilute, in the comparatively inert solvent, water. Molten salts differ from aqueous solutions by the absence of an electrically neutral reference solvent to which the movement of the constituent ions can be referred [35].

Recent developments have widened the scope of the term molten salts to include molten media which may not be wholly ionic or derived from simple salts. However, the majority of melts studied are substantially dissociated in the liquid state and the proton is very much a less important species.

The electrolyte KF.2HF does not easily fit into any of the five categories mentioned above. It is, however, a molten salt in the wider sense of the term. One way of regarding it is as a solution of KF in hydrogen fluoride. Liquid HF on its own undergoes slight ionization:

$$2HF \rightleftharpoons H_2F^{\dagger} + F^{-}$$

for which the auto-protolysis constant is $2 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$ [22]. In the presence of KF, [F...H-F] ions are formed by the development of a hydrogen-bond between a simple fluorine ion F⁻ and a molecule of undissociated HF. Therefore in an electrolyte of KF.2HF there will be an excess of solvent HF, which will play a role similar to water in such areas as the double layer, a description of which follows.

3.4 The Electrode-Electrolyte Interphase

An interphase is a region between two phases where the properties of this region are not yet equivalent to those in either bulk phase. This region is most important as it is here that any reaction occurs.

On placing an electrode in an electrolyte, there is a breakdown of neutrality at the phase boundaries. Two layers of opposite electrical charge are formed which are separated by a few tenths of a nanometer. This is termed the double layer and across this a potential difference exists.

Models of varying sophistication have been proposed in the past. These range from the simple Helmholtz model [38], represented in figure 3.3, which proposed two rigidly held planes of equal charges having purely capacitive behaviour, to a model proposed by Devanathan et al [39]. The Helmholtz model was modified by Gouy [40] and Chapman [41] by introducing the concept of a diffuse layer in the electrolyte where the distribution of ions is a result of the ordering forces of the electrical field and disorder due to thermal motion. The ions are assumed to be point charges which approach to within infinitely small distances of the electrode surface.

The concept was further modified by Stern [42] by allowing the ions a finite volume. Also postulated was a monolayer of ions held at a finite distance from the electrode with a diffuse layer extending into the bulk solution. Grahame [43] proposed an interphase of three layers - a Helmholtz plane divided in two and a diffuse layer, figure 3.4. The inner plane of the Helmholtz layer passes through the centres of specifically adsorbed anions which are unlikely to be solvated and the outer plane passes through solvated cation centres at their plane of closest approach.

The more recent model of Devanathan et al [39] proposes the predominate existance of solvent in the interphase. They suggested that the electrode surface is covered with an oriented layer of solvent

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Charge distribution and potential profile through the Figure 3.3 double layer according to the Helmholtz model [38].



Figure 3.4 Charge distribution and potential profile through the double layer according to the Grahame model [43].



Figure 3.5 Model of double layer according to Devanathan, Bockris and Muller [39].

molecules, which on certain sites are displaced by specifically adsorbed ions which do not carry a solvation shell (Figure 3.5).

At potentials close to the equilibrium potential the behaviour of the molten salt electrode/electrolyte interphase can be comparable with that of an aqueous system [35]. It is generally accepted that molten salts have some kind of a diffuse region, which can be modified to postulate an electrical multilayer [44], where the excess charge on the melt side of a liquid metal-molten salt interphase may be distributed across several ionic layers.

3.5 Mechanisms of Hydrogen Evolution

In the cathodic evolution of hydrogen from acid media:

$$H^{T} + e \rightarrow \frac{1}{2}H_{2}$$
 (3.39)

the particular mechanism involved depends on the electrode material under consideration, the solution composition and the pre-treatment of the electrode surface. There is, however, generally only one type of
intermediate, which is the adsorbed hydrogen atom. Three main steps are assumed to be operative:

(1) The discharge or Volmer process

$$H' + M + e' \rightarrow M-H (ads)$$
 (3.40)

(2) The electrochemical or Heyrovsky process

 $H^+ + H (ads) + e \rightarrow H_2$ (3.41)

(3) The hydrogen atom combination or Tafel reaction

$$2H (ads) \rightarrow H_2 \tag{3.42}$$

Both possible mechanisms involve the formation and cleavage of an M-H(ads) bond and it can be seen that while an increase in the free energy of adsorption favours the formation of M-H, the opposite effect is seen in the cleavage process. Consequently, intermediate values of ΔG_{ADS}^{Θ} favour higher rates of reaction. This can be represented in the form of a "volcano" plot shown in Figure 3.6 [45].



Figure 3.6 'Volcano' plot of the exchange current density for the hydrogen evolution reaction versus the metal-hydrogen bond formed with the metal of the electrode [45].

Any one of the three steps may be rate determining and the nature of this step may vary with overpotential.

(1) Discharge step rate determining

The rate of this step can be written as

$$\vec{v}_1 = \vec{k}_1 C_{H^+} (1 - \theta)$$
 (3.43)

If this step is always slow when compared with (3.41) and (3.42), then θ is small and $(1 - \theta) \rightarrow 1$. The current density for this mechanism may then be written as:

$$I = F k_1 C_{H+} \exp \left(\frac{-\alpha_1 F \eta_1}{RT}\right)$$
(3.44)

and

$$\log I = \log F k_1 + \log C_{H^+} - \frac{\alpha_1 F \eta_1}{RT}$$
 (3.45)

The Tafel slope is then equal to $-2.3RT/\alpha_1F$ mv/decade and the reaction is first order with respect to proton.

(2) <u>Electrochemical step rate determining</u> The rate of this step can be written as

$$\vec{v}_2 = \vec{k}_2 C_{H+} \theta \qquad (3.46)$$

(a) At low overpotentials the current may be obtained by applying a quasi-equilibrium assumption. Thus:

I = 2m F k₂ C_{H+}² exp
$$\left(-\frac{(1 + \alpha_2)F}{RT}\right)$$
 (3.47)

and

$$\log I = \log 2m F k_2 + 2 \log C_{H^+} - \frac{(1 + \alpha_2)F}{RT} n_2 (3.48)$$

where $m = \exp \left(-F \frac{(E_2^{0} - E_1^{0})}{RT}\right)$

The Tafel slope is the $-\frac{RT}{(1 + \alpha_2)F}$ and the reaction is second order with respect to proton.
(b) At high overpotentials θ is obtained by using the approximation $\vec{v}_1 = \vec{v}_2$. Therefore:

$$I = 2F k_2 C_{H^+} K \exp \left(-\frac{\alpha_2 F}{RT} \eta_2\right)$$
(3.49)

and

$$\log I = \log 2F k_2 K + \log C_{H+} -\alpha_2 F \eta_2$$
 (3.50)
 $\frac{1}{RT}$

where the Tafel slope is $-\frac{RT}{\alpha_2 F}$ and the reaction is first order with

respect to proton.

-

(3) Hydrogen atom combination rate limiting

At potentials near to the equilibrium potential θ is obtained as in 2(a) above.

The current is found to be:

$$I = 2 F k_3 \theta^2$$
 (3.51)

or

$$I = 2F k_3 C_{H^+}^2 \exp \left(-\frac{2F}{RT} n_3\right)$$
(3.52)

and

$$\log I = \log 2F k_3 + 2 \log C_{H^+} - \frac{2F}{2.3RT} n_3$$
 (3.53)

The Tafel slope becomes -2.3RT/2F and the reaction is second order with respect to proton.

The conclusions of these treatments are summarised in Table 3.1.

Table 3.1

Rate-determining step	Overpotential range	Tafel slope at 95°C
(1)	all	(73/ α) mV/decade
(2)	low	$(73/(1+\alpha))mV/decade$
	high	$(73/\alpha)$ mV/decade
(3)	low	36 mV/decade

The existence of adsorbed hydrogen on electrocatalytically active metals may be demonstrated by means of cyclic voltammetry. The current observed reflects its formation or ionization (the hydrogen wave) by the Volmer reaction

 $H^+ + e \rightleftharpoons H (ads)$ (3.54)

The hydrogen wave occurs at potentials positive to the reversible hydrogen electrode. The wave usually appears in the potential region between 0 - 0.4V positive to the reversible hydrogen electrode, thus corresponding to underpotential deposition.

The anodic and cathodic waves are almost symmetrical, particularly on Pt. This indicates a very high rate of the Volmer reaction. The charge involved in the hydrogen wave on Pt is generally very reproducible and should correspond to one monoatomic layer of H (ads) - 210 μ Ccm⁻² on Pt [45]. Therefore, it is possible that the Pt surface is fully covered with H (ads) at the reversible hydrogen electrode potential. On other metals, nickel for example, the surface coverage is much smaller than unity due to surface oxidation.

It is possible to observe several peaks in the hydrogen wave, indicating the existence of distinguishable kinds of H (ads) which are of differing chemical stability and reactivity. The feature occurs because of the existence of various crystallographic planes. The shape of the hydrogen wave is not usually reproducible in detail and depends on the previous treatment of the surface.

The method of determining mechanism of hydrogen evolution described above has been applied to a molten salt system by Shams El Din [46]. The system studied was molten KHSO₄ at a range of temperatures (370-670°C). It was proposed that fused KHSO₄ is a very strong acid, apparently due to its ready ionization into hydrogen and sulphate ions. Therefore, the melt is considered to be rich in free H^+ ion. The diffusion of this ion to the cathode is unlikely to be the cause of any polarization. It was further assumed that the hydration of the proton in aqueous systems does not affect the slope of the Tafel plot. Therefore, it is possible to apply the results of the treatment to the evolution of hydrogen from molten KHSO₄.

The paper also quoted the KF.2HF system as an example of a molten salt with one or more ionizable hydrogen ions which is a prerequisite for the cathodic evolution of hydrogen from a molten salt. It would, therefore, seem possible to extend this method to the present study.

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Unfortunately, it is not possible to determine the effect of temperature on the reaction due to the rapid loss of hydrogen fluoride at higher temperatures.

3.6 Gas Evolving Electrode

A detailed review by Vogt [47] has been published and the passage which follows is a summary of the main features.

A gas evolving electrode is characterised by the combined action of two functions. The first is that, as a consequence of an electrochemical reaction, a substance is liberated at the electrode which appears to be dissolved in the liquid adjacent to the electrode. The second is that the electrode causes, by a physical process, the liberation of the dissolved substance from the liquid by the formation of a gaseous phase. Both the electrochemical and physical processes are linked in the overall steady state condition if certain prerequisites are satisfied. Examples of these are that consecutive homogeneous reactions do not occur, gas does not diffuse through and is not absorbed by the electrode and gas is not evolved at any other solid surfaces.

At low current densities of the gas-evolving reaction, the dissolved gas is carried away from the electrode by molecular diffusion and is not transferred into the gaseous phase. At sufficiently high current densities bubbles are formed at nucleation sites at the electrode. This results when supersaturation of the liquid next to the electrode reaches a high enough value and a thermodynamic fluctuation of sufficient magnitude occurs to form a bubble of at least the critical radius, R_C . If a radius of less than R_C occurs the bubble redissolves. Electrode surfaces include pits, scratches and grooves which are never perfectly wetted. These trap gas which can then act as a bubble initiator or nucleus. When a bubble leaves the surface, some residual gas is left which serves as a nucleus for a successive bubble. If, at a given supersaturation, the radius of the interface is smaller than R_C the site is inactive.

In an investigation of supersaturation in the vicinity of hydrogen- and oxygen-evolving electrodes [48] it was observed that a limiting value was reached at current densities of about 1000 Am⁻². It is important to distinguish between the supersaturation governing the nucleation process (i.e. liquid contacting gas evolving electrodes) and the supersaturation governing bubble growth which has much lower values than the former. The number of active nucleation sites in a given area depends on the supersaturation and on the total number of available sites. An increase in roughness of a surface does not necessarily lead to an increase in the number of nuclei as mass transfer may not be accelerated. In addition aging of nucleation sites leads to a loss of activity [49].

Initially the important factors in bubble growth are viscous, inertial and interfacial forces. At large diameters the rate of mass transfer of dissolved gas is important and other factors can be neglected. The initial growth of bubbles is very slow but after a short period a transition to asymptotic growth occurs.

Any formulated growth laws apply only to cases where adhering bubbles do not interefere, i.e. limited to moderate current density only. One anomaly is the jump-off of two bubbles of similar size during coalescence which may occur immediately two bubbles touch. The resulting bubble leaves the electrode and immediately returns to become reattached. Another form of coalescence occurs when large bubbles slide up the face of the electrode and "scavenge" smaller bubbles.

The growing bubble adheres to the surface until it reaches a size at which the adhesion forces resulting from interfacial tension are exceeded by buoyancy and shear forces, figure 3.7.

The interfacial tension at the electrode-electrolyte interface depends greatly on the electrical potential. As the interfacial tensions at the solid-gas and gas-liquid interface remain almost constant the contact angle must change with the electrical potential. At a metal or graphite electrode, faced horizontally upward or vertically, the bubble departure diameter, d, is of the order of 50 μ m, depending on polarity, the electrolyte solution, current density and liquid bulk flow velocity. Departure diameters are very much larger in molten salts, being of the order of 1 mm.

Mass transfer is affected considerably by the processes associated with the formation and detachment of bubbles. The following effects are the main influences:

(1) Penetration Effect

A detached, rising bubble transfers momentum to the surrounding liquid causing a flow wake to develop. Liquid from the outer edge of the concentration boundary layer is brought to the electrode surface causing the liquid adjacent to the electrode to be periodically replaced. The model assumes that a solution having the concentration

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₽ pressure of liquid phase
Pg pressure of gaseous phase
F adhesion force
Y_{sg} solid/gas interfacial tension
Y_{sL} solid/liquid interfacial tension
♦ Contact angle
Y_{Lg} liquid/gas interfacial tension

Figure 3.7 Balance of static forces acting on an idealized bubble adhering to a horizontal surface.

of the bulk reaches the electrode after the bubble has departed and that mass transfer is governed by non-steady-state diffusion during the time before the next bubble starts to grow.

(2) <u>Microconvection Effect</u>

While the growing bubble adheres to the electrode, the solution is pushed past the electrode in centrifugal directions. A microconvective flow regime develops in the vicinity of the bubble. This model assumes convective mass transfer alone to be active, diffusion being ignored.

(3) Hydrodynamic or Macroconvection Effect

A group of bubbles rising to the surface causes convective liquid flow which is not directly related to the two effects above. This twophase flow results in flow velocities which can interfere with other effects. The hydrodynamic model takes into account the electrolyte flow caused by this lifting effect and considers it to be the governing factor in mass transfer.

3.7 Effect of Gas Evolution on Electrode Performance

The main effects of gas evolution on the performance of a gas evolving electrode are [50]:

(1) Ohmic obstruction within the electrolyte.

(2) Area masking on the electrode surface which raises surface overpotential by increasing the effective current density.

(3) Decreased local supersaturation, which lowers the concentration overpotential.

It should be noted, however, that the latter factor only occurs with cathodes of high catalytic activity, where there is a departure from Tafel kinetics. In these cases a net depolarization of the electrode can be achieved.

Much attention has been directed towards the increase in bulk electrolyte resistivity caused by dispersed bubbles as the electrical conductivity of gas is practically equal to zero. The effective conductivity of an electrolyte uniformly filled with gas bubbles may be estimated by two main equations - the Maxwell equation [51] and the Bruggeman equation [52].

There also exists a thin layer of electrolyte close to the electrode surface which is known to be more crowded with bubbles than the bulk electrolyte. The phenomenon of locally obstructed gas removal is known as "bubble curtain" effect. Efforts have been made to characterise this layer in both experiments and theoretical studies. Kuhn and Stevenson [53] made current-potential measurements at gasevolving anodes and cathodes in sulphuric acid. In non-steady-state measurements, the ohmic drop component of the total voltage was isolated. Their results suggested a substantial ohmic component on or close to the electrode surface. Janssen and various co-workers [54, 55] have also studied the bubble effect on the ohmic resistance of a thin solution layer at a gas-evolving electrode by both current interruption and a.c. impedance methods. A dimensionless correlation for ΔR_{im}^* (the increase in the resistance of the solution layer between diaphragm and working electrode due to bubbles, divided by the resistance of this layer in the absence of bubbles) was obtained, which included various parameters relating to the geometry of the cell and the nature of the gas and electrode. An interesting observation was that ΔR_{int} is independent of current density in the range studied. It was also noted that a difference exists in the coalescence behaviour of oxygen and hydrogen, allowing two types of gas-evolving electrodes to be distinguished. For each type a model describing the mass transfer of indicator ions to the gas-evolving electrode is given [56, 57]. A further practical study was completed by Gallone et al [58]. Anodic and cathodic polarization curves were determined in KOH at a range of temperatures. They adopted the electronic current interrupter technique with the Luggin capillary either inserted from behind (i.e. at zero distance), or at a distance of 3 mm from the electrode. They also reported large resistance values localized on the electrode surface. As to the nature of the ohmic term, a number of conjectures were made. They disputed that the "bubble curtain" adhering to the gas evolving surface was the main source of ohmic polarisation. The fractional coverage shielding a portion of the electrode surface increases with current density. Consequently the true current density on the remaining surface gradually increases to more than its nominal value. Should this phenomenon be important, the overvoltage curve obtained after IR correction would no longer show Tafel linearity. In fact their findings confirmed Tafel linearity.

Furthermore, calculations based on average bubble radius and fractional coverage [56, 59] give results which are more than one order

of magnitude less than values obtained experimentally. The bubble curtain resistance should increase with current density a fact contradicted by their results, where a constant superficial resistance was observed.

In view of these facts alternative theories were proposed. In the case of oxygen evolution there is the possibility of the formation of a resistive oxide layer. However, it was not confirmed by ohmic drop measurements carried out in a dry cell that such a layer would provide sufficient resistance. Also, this proposal was not considered tenable for cathodic hydrogen discharge.

Another hypothesis concerned the build up of an adsorbed gas layer presenting a definite ohmic resistance. Such layers may be detected by galvanostatic potential-transient methods. They reported that Shibata [60] measured the formation of an oxygen film beyond monolayer thickness after anodization of smooth Pt at 50 mAm⁻² for 20 s. It was concluded that it was reasonable to assume that the multilayer thickness can reach a limiting value at relatively low current density and in a relatively short time.

The increment in resistance due to the surface layer of bubbles has been estimated using bulk dispersion models such as the Maxwell and Bruggeman equations. Janssen and Barendrecht [54] found that $\log \Delta R^* = a_1 + b \log i$ (where $\Delta R^* = (R - R_0)/R_0$, R = ohmic resistance of a solution layer at the working electrode and $R_0 = R$ at i = 0). Vogt [61] presented a hydrodynamic model of a cell with gas evolving electrodes where the major assumption was that the ohmic resistance of the dispersion of gas bubbles in electrolyte can be separated into two parts; a stagnant boundary layer at the electrode being enriched in gas, and a flowing bulk in the centre region. This model would seem to be in agreement with the findings of Gallone et al [58].

Tobias [62] proposed useful approximations for treating concentrated, random suspensions of spheres and applied these results in the evaluation of the effect of gas bubbles on the resistance and current distribution in electrolytic gas generators. Hine et al [63] differentiated between a relatively concentrated dispersion of gases near the electrode and the more dilute suspension in the bulk electrolyte.

Sides and Tobias [64] presented an analytical solution for the primary potential and current distribution around a spherical bubble in contact with a plane electrode. The current density is zero at the point of contact of the bubble and reaches only 1% of its undisturbed value at 30% of the radius from that point. They also point out that

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attached bubbles cause less obstruction than free bubbles since the field disturbance due to an attached bubble is truncated by the isopotential electrode surface.

The bubbles were considered to be arranged regularly in a single layer and they obtained an expression for ΔR , the addition to the ohmic interelectrode resistance calculated in the absence of bubbles. A simple approach to this model is to assume that at any plane parallel to the electrode surface the current density through the unvoided electrolyte is uniform. However, in this treatment a further resistance was introduced, occasioned by the pinching of the field in the neighbourhood of bubbles sited close to one another, as well as a fractional electrode coverage. Lanzi and Savinell [65] also presented a modification of the simple approach where the electrolyte among the attached bubbles is taken as a 3-dimensional dispersion of smaller bubbles. This was developed from a two-dimensional constriction model of a dense bubble curtain. Vogt [66], however, considered this unnecessary as ΔR may be satisfactorily estimated by using the more conventional approach of assigning an effective conductivity to the layer comprising the bubble curtain.

Hine and Murakami [67] measured the superficial resistivity of the solution containing bubbles, which agreed well with the Bruggemann equation, whilst Sigrist et al [68] found good correlation between effective conductivity and the gas voidage with the Maxwell equation.

The use of expanded metal electrodes to decrease the ohmic resistance is also detailed. Elsner and Coeuret [69] report on an experimental study of gas-evolving expanded metal electrodes. They observed the variations of the cell voltage with the electrolyte velocity and current density for different orientations of the mesh with respect to the electrolyte flow direction. They concluded that the cell voltage depended on the orientation of the mesh and that certain orientations allow the deflecting of the gas towards the rear of the electrode but at the same time coalescence of bubbles and the immobilization of big bubbles are facilitated.

Leroux and Coeuret [70, 71, 72] have completed detailed studies of current and potential distribution and mass transfer at flowthrough electrodes of ordered sheets of expanded metal. The influence of mesh size, mest orientation with respect to the electrolyte flow direction and the respective arrangement of the sheets are studied. In conclusion, they recommend a particular orientation of the grids and a small mesh size to guarantee a high mass transfer coefficient. Jorne and Louvar [73] observed that, while gas evolution enhances mass transfer of reactants to and from the electrode surface, the presence of bubbles can lead to increased ohmic drop and non-uniform current distribution. They tested the effectiveness of gas-diverting electrodes as a function of spacing between the cathode and membrane, the current density, the temperature and the geometry of the electrode. They reported an increase in current efficiency due to induced turbulence and that restrictions on cell height are removed.

Hine and Murakami [74] investigated the effect of bubbles on terminal voltage, solution i-R drop and overvoltage in a vertical cell with perforated electrodes. They report that, while cell voltage can be minimized, the reduction in surface area is an important disadvantage. From the experimental results obtained the optimum perforation was estimated to be in the range 5-15%.

3.8 Linear Potential Sweep/Cyclic Voltammetry

The technique of potential sweep can be used to give detailed pictures of charge transfer systems and reaction mechanisms. The basis of the technique is to apply a linear potential/time function to an electrode, observing the subsequent current response. If the electrode potential is simply swept from one limit to another at a given sweep speed, v, and the potential sweep halted, it is termed linear sweep voltammetry. If the electrode potential, having reached the second limit is reversed and swept back to the first limit, this is termed cyclic voltammetry. After returning to the first limit, the sweep may be halted, reversed again or continued to a third potential limit.

The current-voltage trace obtained can be viewed as an "electrochemical spectrum", the shape and position of any current peaks being determined by solution composition, concentration, electrode material and sweep rate. Slow sweep rates are employed for "steady-state" current-voltage curves, where it is assumed that the surface relaxes sufficiently rapidly for the surface to approach a true steady-state. Higher sweep rates are used to test the existence of short lived intermediates. Any peak in this instance is the result of mass transfer and the progressive depletion of the electroactive species at the electrode.

Accurate kinetic parameters can only be derived from linear potential sweep experiments as the equations derived for the technique apply to situations where there is not concentration gradient in the solution prior to the start of the sweep. Complex concentration gradients commonly arise during cyclic voltammetry. As a result this technique is more

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suited to the identification of steps in an overall reaction and to the detection of new species appearing during electrolysis. Cyclic-voltammetry is used, therefore, in the qualitative evaluation of intermediates.

For a simple electron transfer process an increased sweep rate (v) causes an increase in peak current density (i_p) at the corresponding peak potential (E_p) . The Nernstian equilibrium at the electrode surface is maintained if the electron transfer is sufficiently high. The peak current density for a cathodic sweep then follows the Randles-Sevčik relationship:

$$i_p = -0.4463 \text{ nF} \left(\frac{nF}{RT}\right)^{\frac{1}{2}} \cdot D^{\frac{1}{2}} \cdot C_0^{\infty} v^{\frac{1}{2}}$$
 (3.55)

where n is the overall number of electrons transferred in the electrode process, D is the diffusion coefficient $(cm^2 s^{-1})$, C_0^{∞} is the concentration of the oxidised species in the bulk solution (mol cm⁻³), i_p is the peak current density (A cm⁻²), and v is the sweep rate (Vs⁻¹). Thus, the peak current density is proportional to the square roots of both the sweep rate and the diffusion coefficient and directly proportional to the concentration of electroactive species.

In the case where the reaction is slow in comparison with sweep rate the Nernstian response cannot be assumed. In this case the peak current density is also proportional to the square root of the transfer coefficient.

3.9 Cyclic Voltammetry and Surface Processes

In the case where peaks on a cyclic voltammogram are not caused by a process in which all reactants and products are freely soluble, a surface process may be involved, such as adsorption, metal deposition and corrosion. Where adsorbed species are the only electroactive components the behaviour of the peak current and peak shape will differ from that described above. The peaks are sharp and symmetrical, there is little or no peak separation and the charges associated with anodic and cathodic peaks should be equal. The actual values of I_p , E_p and the peak width depend on the type of adsorption isotherm involved and the relative strengths of adsorption of the oxidised and reduced species. Where adsorption is described by a Langmuir isotherm the peak cathodic current density is given by:

$$I_{p} = \frac{n^{2} F^{2} \Gamma_{0}}{4 RT} v$$
 (3.56)

where Γ_0 is the surface excess of the oxidised species before the sweep. Hence, the peak current is directly proportional to the sweep rate.

In the case where both adsorbed and solution species are electroactive, the current associated with the adsorbed species appears as a pre- or post-peak, depending on the relative strength of adsorption of products and reactants. Strong reactant adsorption results in a postpeak and strong product adsorption in a pre-peak. The solution peaks will increase in height in proportion with $v^{\frac{1}{2}}$, whilst pre- and postpeaks increase directly with sweep rate. Furthermore, solution peak height will increase linearly with concentration, whilst adsorption peak height will increase with concentration (but not necessarily linearly) until reaching a limiting value at complete surface coverage.

CHAPTER 4

EXPERIMENTAL METHODS

4.1 The Electrolytic Cell

The basis of the electrolytic cell consisted of a 500 ml poly-(methylpentene) (PMP) beaker into which varying electrode assemblies were fitted. The PMP beaker (Azlon Products) could be used at temperatures up to approximately 180°C, was resistant to hydrogen fluoride and had the advantage over PTFE of being transparent, allowing the system to be observed during operation.

Two types of lid were designed and machined. The first was intended for use with a simple 1A cell used in the initial investigations. This was machined from a $\frac{1}{4}$ " PTFE sheet and sat on the lip of the beaker. The lid supported the cell components which included a mild steel cathode, two PTFE shrouded porous carbon anodes and a reference electrode holder (Figures 4.1, 4.2, 4.3).

The cathode for use in the simple 1A cell was pressure vessel grade mild steel (BS 1501), supplied by BNFL and used in plant cell cathode plates. The dimensions were 66 x 24 x 8 mm and were chosen to allow operation at a current density approximate to that reported for industrial cells [2]. This was held in the central position in the lid.

The two counter electrodes were of Schumacher Carbo 30G porous carbon, again supplied by BNFL. The physical properties of this carbon are shown in Table 4.1. Impurities contained within the carbon are sulphur, lead, iron, potassium, chromium, copper and nickel. These were prepared for the cell by washing with trichloroethylene to remove organic matter, 10% hydrochloric acid, distilled water and then drying at 100°C. Electrical contact was made by a ring of copper foil which fitted round the top most part of each anode rod. Each anode then sat on a flange within the PTFE shielding, leaving a radial gap of 5 mm round the anode. Both anodes protruded approximately 2.5 cm from the bottom of the shielding, the purpose of which was to separate the product gases which can react explosively if allowed to mix. The PTFE chimneys fitted tightly over the shielding and the copper contact was fed out under this. The two anodes then fitted, one on either side of the cathode into the lid.



А

Figure 4.1

Components of 1A cell.

- A Anode shield and chimney (PTFE).
- B Reference electrode holder (PTFE).
- C Porous carbon anode.

All approximately to scale.

Figure 4.2

Components of 1A cell.

D Spade type cathode.

E Modified screw in cathode with support (PTFE).

F Cell lid (PTFE) 1. Position of anodes.

- 2. Position of cathode.
- 3. Position of reference electrode.
- 4. Vent hole.

All approximately to scale.





1 AMP LABORATORY CELL

Figure 4.3 Diagram of assembled 1A cell.

TABLE 41

TYPICAL PHYSICAL PROPERTIES OF CARBO 30G

3 3
s-1

*Measured on the flow rate of nitrogen in $m^3 s^{-1}$ passing through 1 m^2 of specimen 2.5cm thick under a pressure of 5cm water gauge.

The reference electrode was Pd/H_2 which was prepared in the following manner. The end of a 0.5 mm diameter Pd wire (99.99% purity, Koch Light Ltd.) was formed into a ball of about 1 mm diameter by heating in a reducing flame. The electrode was then charged with hydrogen in the KF.2HF melt. The uptake of hydrogen causes the Pd to undergo a phase transition when the H_2/Pd ratio exceeds 0.6:

$$\alpha - Pd + H_2 = \beta - Pd (H_2)$$
 (4.1)

The charging was carried out with a D.C. power pack (Thurlby PL320) for 6 hours with a charging current of 5 mA. The electrode was then allowed to rest overnight to allow it to stabilise. The palladium vire was held in a PTFE unit with a crude Luggin probe that was positioned close to the cathode.

This electrode is a hydrogen electrode and all electrode potentials are reported relative to it. However, it is not a standard hydrogen electrode since the activity of H^+ in the melt will not be unity. Without the autoprotolysis constant of HF in the electrolyte at 95°C an estimate of the electrode potential relative to a SHE is impossible [75].

The second type of electrode assembly was designed for use with a smaller cathode. The reference electrode holder and the anode assembly were interchangeable with the design described above. A ring of PTFE was machined from $\frac{1}{2}$ " PTFE and fitted tightly into the top of the beaker. Into this was inserted the stepped PTFE lid allowing overlap with the edges of the ring.

The cathode was a dsic of mild steel machined from an 8 mm plate, which was then screwed into a PTFE support in a vertical orientation. The diameter of the electrode was 15 mm and the electrical connection was made to the back via a channel leading from the top of the support to the screw thread. A nickel electrode of the same type was also prepared.

Other cathodes used were of a rod type which were inserted into the cell via and supported by the vent tubes. These were used in galvanostatic experiments and were of mild steel, lead, nickel, platinised mild steel and electroless plated nickel on steel. The platinised mild steel electrode was prepared by a three second dip in chloroplatinic acid. The electrode of electroless plated nickel on steel was prepared by using a commercially available plating mixture.

The electrolyte, except where otherwise stated, was industrial grade KF.2HF as supplied and used by BNF plc. It was delivered in a

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conditioned (pre-electrolysed) state with a high level of HF. A typical analysis, supplied by BNF plc. is:

HF	43.4	4% w/w
H ₂ 0	0.09	9% w∕w
Fe	450	ppm
Ni .	41	ppm
Cu	<5	ppm
РЪ	180	ppm

The heater unit was a modified chromatographic oven with a well in which the beaker sat. A window was cut into the front of the unit which allowed the cell to be observed when illuminated from the rear. The oven generally operated at 95°C and was fitted with a thermal cutout which prevented operation at temperatures above 150°C.

750 g of solid electrolyte were placed in the PMP beaker and covered with a plain PTFE lid. This was then placed in the heater unit. When first molten the electrolyte was opaque but after one or two days became very clear. The plain lid was then replaced with the electrode assembly.

4.2 Electrical Equipment

A Thompson Ministat potentiostat (0.20 V, 0-15 A) was used throughout the project. Potential-time ramps were produced by either a Thompson Precision "16 bit" ramp generator or a Kemitron function generator which also incorporated a pulse unit. A Bryans 26000 X-Y chart recorder was used to record current-potential data and a BBC Y-t recorder for current-time data.

4.3 <u>Preparation of Pure Electrolyte</u> (or "much ado about nothing") Potassium bifluoride (GPR grade, BDH) was obtained and purified by recrystallisation from tri-distilled water. Potassium bifluoride (300 g) was added to distilled water (350 ml) in a PMP beaker, covered with a PMP watch glass and heated. If necessary the solution was mixed with a polypropylene-coated stirring rod. When all the solid was dissolved, the potassium bifluoride was allowed to crystallise in an ice bath. When crystallisation was complete the solid was filtered off using a polyethylene Buchner funnel and polypropylene Buchner flask. The crystals remaining were redissolved in distilled water (200 ml) and allowed to crystallise. Again the mixture was filtered by Buchner funnel and washed with analar acetone (Fisons). Potassium bifluoride remaining in solution was salted out with acetone and filtered. The crystals were then dried, at approximately 100°C in the heater unit used for other experiments until a constant weight was acheived.

The apparatus for addition of hydrogen fluoride to potassium bifluoride is shown in Figure 4.4. The valves and tubing were of PTFE (Production Techniques) and the mixing bottle of polypropylene with a PTFE bung through which the tubing passed. The nitrogen (OFN, BOC) was fed into the system through a non-return valve and into the mixing bottle. Hydrogen fluoride (Fisons) passed through a fine control needle valve into the mixing bottle. A coarse control valve regulated the flow of gas from the mixing bottle through a bulkhead coupling into a PMP beaker with a tightly-fitting lid of PTFE.

Owing to the bulky nature of the recrystallised potassium bifluoride its addition to the beaker was completed in stages. The beaker was filled with potassium bifluoride and a perforated, inverted PMP beaker connected to the tubing was inserted. The lid was fitted and the beaker placed in the heater unit at 90°C. The system was then flushed with OFN and the nitrogen then shut off. The hydrogen fluoride cylinder was gently warmed with a hot air blower and hydrogen fluoride gas was fed into the beaker. On this addition the potassium bifluoride started to dissolve and its volume decreased, allowing the further addition of the crystals.

Percentage hydrogen fluoride was determined by removing approximately 1 g of electrolyte, using a short length of PTFE tubing with a rubber teat on one end. The sample was placed in a PMP beaker, weighed and dissolved in 200 ml tri-distilled water. This solution was then titrated with 1M NaOH solution using phenolphthalein as indicator and the percentage hydrogen fluoride calculated.

Originally difficulty was experienced in obtaining electrolyte of a sufficiently high hydrogen fluoride level. Electrolyte with 39% HF was satisfactory for cyclic-voltammetry experiments but not for galvanostatic experiments, where polarisation occurred. Consequently the technique was modified by cooling the beaker in an ice/water slurry. This method proved very time consuming but at least yielded electrolyte of a suitable composition.

Analysis of metallic impurities was again performed by BNF plc. and this is the analysis of a typical batch of electrolyte:



A NONRETURN VALVE B FINE CONTROL NEEDLE VALVE C COARSE CONTROL NEEDLE VALVE D HF CYLINDER E MIXING BOTTLE F BEAKER WITH KF.HF

Figure 4.4 Apparatus for addition of HF to recrystallised KF.HF in preparation of purified electrolyte.

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Fe	12 ppm
Ni	<10 ppm
Cu	<5 ppm
Pb	20 ppm
Cr	<5 ppm

.

CHAPTER 5

INITIAL INVESTIGATION OF HYDROGEN EVOLUTION IN KF.2HF

5.1 Preliminary Observations of IA Cell

On first placing the mild steel cathode in the electrolyte small bubbles were seen to be evolved from the electrode. Furthermore, on initial polarization into the hydrogen evolution region, a fine white powder was discharged from the electrode. This collected at the bottom of the cell and after a short time the discharge ceased. These phenomena were attributed to the following equilibrium:

$$Fe + 2HF \iff FeF_2 + H_2$$
 (5.1)

 FeF_2 being a white powder. An open circuit potential of approximately -210 mV versus Pd/H₂ was established.

Cyclic voltammograms of mild steel in industrial electrolyte were obtained with varying potential limits. Figure 5.1 shows a voltammogram with a sweep speed of 10 mVs⁻¹ in the range -0.1V to -1.0V versus Pd/H_2 . Hydrogen evolution occurs at potentials more negative than -400 mV on the forward sweep. Also present on the reverse sweep are two oxidation peaks which were considered to be indicative of the removal of metallic impurities, deposited whilst in the h.e.r. region. It is known that the electrolyte contains easily detectable amounts of iron, lead and nickel, which are present as impurities from the preparation in industrial type cells. It is also known that Ni should have little effect on the cathodic process as it is present in the form $[NiF_6]^{2^-}$. This has a red colouration [76] and it is interesting to note that a mild steel electrode may take up a pink/red colouration if stood in the electrolyte at open circuit for some time. Iron and lead fluorine complexes are not common. Tetrahedral FeF_4 does not seem to exist, although CsFeF₄ appears as a result of the $FeF_6^{3^-}$ octahedrals sharing F^{-} ions. $FeF_{6}^{3^{-}}$ ions are known in the solid state but only species with fewer fluorine atoms occur in solution. However, any existing complexes will not be intensely coloured, the disappearance of colour on addition of fluoride ions being a qualitative analytical test for certain complexes.



Figure 5.1Voltammogram of mild steel in industrial KF.2HF.Sweep speed = 0.01 Vs^{-1} .Potential limits:- $0.10 \text{ V} \rightarrow -1.0 \text{ V}$ vs Pd/H2

By changing the anodic limit of the voltammogram the effect of the deposited metallic impurities on the cathodic current was observed. Figure 5.2 shows a voltammogram with potential limits of -290 mV and -1000 mV versus Pd/H_2 , i.e. only one of the impurities is removed from the electrode on the reverse sweep. This causes the reduction of the cathodic current to about half its value in Figure 5.1. Figure 5.3 shows a voltammogram with the potential limits -370 mV and -1000 mV, i.e. both impurities remain on the electrode throughout the sweep. It can be seen that the cathodic current is virtually the same as in Figure 5.2, the only difference being the exclusion of both peaks.

Simple potentiostatic experiments emphasised the effects of impurities. An electrode which had previously been held in hydrogen evolution, to allow the build up of impurities on the electrode surface, was pulsed from a potential cathodic of both peaks to -1000 mV versus Pd/H_2 . The current/time response is shown in Figure 5.4. The behaviour was compared with that of a clean electrode pulsed to the same potential (Figure 5.5). The latter showed an initial peak followed by a slight drop and finally shows a voltammogram with potential limits of -0.290 V and -1.0 V versus Pd/H_2 , i.e. only one of the impurities is removed from the electrode on the reverse sweep. This causes the reduction of the cathodic current to about half its value in Figure 5.1. Figure 5.3 shows a voltammogram with potential limits of -0.370 V and -1.0 V, i.e. both impurities remain on the electrode throughout the sweep. Ιt can be seen that the cathodic current is virtually the same as in Figure 5.2, the only difference being the exclusion of both peaks.

Simple potentiostatic experiments emphasised the effect of impurities. Figure 5.4 shows the current-time response of a clean electrode pulsed to -1.0 V versus Pd/H_2 . The response of a pre-cathodised electrode (Figure 5.5) differs in that the initial current is approximately half that for the clean electrode. However, both electrodes eventually show similar current densities. This implies that the deposit of impurities, possibly including lead, depresses hydrogen evolution. The higher initial current seen for a clean electrode may also be partially caused by the nucleation of the impurities.

During the course of these simple experiments observations were made on the nature of the bubbles. (This will be referred to several times in the course of the thesis and, therefore, the photographic evidence is collected into one chapter towards the end to allow easier comparison of varying conditions.) On commencing electrolysis at the

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Figure 5.3 As Figure 5.2, except

Potential limits: $-0.35 V \rightarrow -1.0V$

vs Pd/H₂



Figure 5.4Current/time response of clean mild steel electrode inindustrial electrolyte.E = -1.0 V vs Pd/H2.

Pulse from rest potential to - 1.0V vs. Pd/Hz



Figure 5.5Current/time response of pre-cathodised mild steelelectrode in industrial electrolyte.E = -1.0 V vs Pd/H2.

mild steel electrode the bubbles were small, spherical and streamed freely from the electrode. However, as the electrolysis progressed it appeared that fewer nucleation sites were in operation and the bubbles were larger with diameters of 2-3 mm. Furthermore, they became distorted by buoyancy forces, with contact angles at the lower point of contact of more than 90° .

Concurrent with the change in bubble characteristics, there was a build up of impurities on the electrode surface. This was demonstrated by operating at a given potential for some time and then sweeping the electrode potential back through the open circuit potential and recording the current response. Large anodic peaks were obtained at the potentials observed previously. Furthermore, flakes of material were seen to fall from the electrode. When the potential was returned to the hydrogen evolution region a mixture of bubble sizes were observed. Large bubbles were evolved from the covered areas of the electrode and smaller bubbles from the areas clear of any deposit.

The observation of increase in bubble size and contact angle was also recorded by Rudge [2] although no explanation was offered. From these experiments it would appear that there is a link between deposition of metallic impurities and the increase in bubble size. It is also possible that the impurities affect the overvoltage by forming a new surface on the electrode. This may increase the surface area but may also have higher overvoltage requirements.

5.2 Galvanostatic Studies on a Variety of Electrode Materials

Electrodes of mild steel, lead, nickel, electroless nickel plated on steel and platinised mild steel were operated at 40 mA cm⁻² in industrial electrolyte. Both rod type and flat electrodes were used to compare the nature of bubbles on the two electrode geometries.

The potential-time profiles of corresponding electrodes in each set were similar although in general the rod type electrodes showed greater potential noise due to bubbles leaving the electrode. However, there was no readily visible difference in bubble type

The potential-time profile is shown in Figure 5.6. There is an initial peak in potential, a slight fall and then a prolonged increase to give a more or less stable value after about eight hours. Also apparent is an increase in potential noise which is indicative of the gradual increase in bubble size and contact angle.

Both the nickel and electroless plated nickel electrodes showed a higher initial overvoltage and very much larger potential noise, (Figures 5.7 and 5.8). However, with continued operation the over-



Potential/time response of mild steel electrode in Figure 5.6

> / hours t





t / hours

voltage dropped to give a value after two or three hours similar to that for mild steel. In addition there was a marked decrease in potential noise. The type of bubbles present at the start of electrolysis were very different from those evolved from mild steel. They were 4-5 mm in diameter and extremely lenticular with contact angles greatly in excess of 90°. These bubbles were not released from the electrode but skimmed up the surface. As the electrolysis progressed the bubbles became much less lenticular, with a smaller contact angle and were similar to those evolved on mild steel after a similar period of operation.

Lead is a notoriously non-catalytic metal and would, therefore, be expected to require the largest overvoltage. Indeed, it showed the largest initial potential peak, (Figure 5.9), but the overvoltage decreased in a series of steps to give a final value similar to that for mild steel. The bubbles evolved on lead showed none of the extremes of behaviour observed on mild steel and nickel and the potential noise virtually disappeared after about 3 hours of operation.

Platinised mild steel showed great activity for hydrogen evolution, functioning at a very low overpotential for about 30 minutes. However, a marked increase in overpotential occurred after this time to give a final overvoltage similar to that for mild steel, (Figure 5.10). The bubble characteristics showed a similar pattern to mild steel.

5.3 Investigation of the Electrode Deposit

After two to three hours operation it is possible to see a deposit on the electrode which consists of a smooth layer firmly attached to the electrode and a more porous layer of small dendrites on top of this. Figure 5.11 shows the surface of a mild steel electrode after 3 hours operation at 100 mA cm⁻² and then washed to remove any electrolyte.

To test for the presence of metallic impurities in the deposit, the new surface of the electrode was analysed by EDAX. Some problems were encountered because of the large amounts of potassium present in the solidified, adhering electrolyte, which could mask the peaks of less abundant metals. The electrolyte may be washed away but there is also a risk of removing the deposit itself. Nevertheless, it is apparent from the spectra of mild steel, nickel and lead electrodes (Figures 5.12, 5.13 and 5.14) that lead and iron are present in the deposited layer. From a wavelength dispersive analysis, performed by the electron probe microanalyser, it seems that the two metals are present in more or less equal quantities and make up the majority of the deposit. A very low level of nickel (3%) was detected on the mild



Potential/time response of lead electrode in industrial Figure 5.9

t / hours



Figure 5.10 Potential/time response of platinised mild steel

t / hours


Figure 5.11 Deposit on mild steel electrode after operating at 0.10 Acm^{-2} for 3 hours. Magnification x 6.3,



<u>Figure 5.12</u> EDAX analysis of deposit on mild steel electrode after operating at 0.30 Acm^{-2} for 3 hours.





<u>Figure 5.14</u> EDAX analysis of deposit on nickel electrode after operating at 0.30 Acm⁻² for 3 hours. Note large potassium peak due to inadequate washing of deposit. steel electrode indicating that small amounts of the metal may be present in forms other than the complex $[NiF_6]^{3^-}$.

5.4 Discussion

5.4.1 Influence of electrode material on overvoltage

The bulk electrode material certainly has a large influence on overvoltage at the start of electrolysis. As expected, lead shows the largest overvoltage and platinised mild steel showed the greatest activity for hydrogen evolution. However, after three or four hours all electrodes show similar overvoltages. In the case of platinised mild steel the change in activity is probably linked with the active sites of platinum being covered by deposited impurities. For nickel and lead electrodes, the activity appears to be increased by the deposition. This implies that, apart from the first 30 minutes of electrolysis, the active surface for hydrogen evolution is no longer the bulk electrode but becomes the deposit. This explains why all electrodes eventually show very similar overvoltages despite their widely differing initial behaviour.

5.4.2 Influence of electrode material on bubble characteristics

The bulk electrode material appears to have a great influence on the type of bubbles produced. The two extreme cases seen in this study are nickel and mild steel. Nickel electrodes produce very large, lenticular bubbles at the start of electrolysis which interfere greatly with electrolysis, almost forming a visible gas film over the electrode surface. These bubbles, however, decrease in size as impurities are deposited and at least part of the decrease in operating overvoltage for nickel may be attributed to the improved bubble characteristics. In comparison, mild steel produces small spherical bubbles at the start of electrolysis which increase in size with time.

That the metallic deposit is responsible for the changes seen is almost certain. Where a mild steel electrode has areas that are uncovered, small bubbles are evolved. Where the electrode is covered, large bubbles are evolved.

That there is a difference between the bubble evolving characteristics of nickel and steel has been reported by Elsner and Coeuret [69]. In a study of potential distribution along expanded metal electrodes, nickel and steel electrodes were used. They reported that the cell voltage was higher for stainless steel and attributed this to the bubbles evolved on the materials having different characteristics and, in particular, different diameters. Unfortunately, no further details were given other than the solution potential distributions being very different for the two. They reported poor reproducibility during their experiments particularly for stainless steel. However, they draw the qualitative conclusion that the superficial state of the electrode changes during an experiment, particularly with nickel. It is on this superficial state that the distribution of nucleation centres and the growth of bubbles both depend directly. This is doubly so in the case of the present study as the surface is modified still further by deposition of impurities.

These observations on gas evolution tend to imply that the presence of bubbles has an adverse effect on bubble evolution. In the case of nickel the overvoltage decreases as bubble size and, hence, potential noise decrease. Mild steel shows a lower overvoltage when small bubbles are evolved than when larger ones are produced. The effect may not be solely due to the bubbles as there is probably an increase in surface area as well but it is impossible to separate the two factors.

The increase in ohmic potential drop due to the presence of gas bubbles is a well documented phenomenon in other systems but has not been investigated in KF.2HF. The system presently under study differs from many other industrial installations in that it is not practically possible to circulate the electrolyte. Thus bubbles are only released when buoyancy and shear forces in the static electrolyte outweigh the adhesion forces resulting from interfacial tension. Another difference is that the hydrogen evolution current density is fairly low at approximately 40 mA cm⁻², while other gas producing electrodes are expected to work at current densities as high as 1 A cm⁻².

5.5 Conclusions

(1) The active surface for hydrogen evolution is the bulk electrode for only a relatively short period of operation. After this the deposit of impurities becomes the active surface. Therefore, the choice of cathode material can be based almost solely on cost. (2) The deposit on the electrode material improves the overvoltage characteristics of lead probably by the deposition of iron. There will also be an increase in surface area which is beneficial too.

(3) The metallic deposit affects the bubble characteristics causing intermediate sizes to predominate. In the case of mild steel this has an adverse effect, as in the absence of the deposit small bubbles are formed. In the case of nickel the performance is improved by decreasing bubble size.

CHAPTER 6

ELECTROCHEMICAL INVESTIGATION OF HYDROGEN EVOLUTION ON PLATINUM AND MILD STEEL

6.1 Study of Platinum in KF.2HF

6.1.1 Introduction

Doughty et al [77] have published a study of fluorine evolution on platinum in anhydrous hydrogen fluoride at 0°C. In steady state experiments it was shown that log i-E graphs have a linear portion and that the Tafel slope is $(240 \text{ mV})^{-1}$. The recorded cyclic voltammograms between 0 V and 3.0 V vs Pd/H₂ showed two oxidation peaks prior to fluorine evolution and a single reduction peak on the reverse sweep. The peak height of the latter varied linearly with sweep rate and therefore the process was suggested to be the reduction of a fluoride layer. The second oxidation process is probably the further, highly irreversible oxidation of the platinum fluoride layer formed in the first oxidation process.

The evolution of hydrogen on platinum in KF.HF at 250°C has been studied by Pizzini and various co-workers [33,34] as mentioned previously. In mainly steady-state experiments they investigated the effect of varying amounts of water. In some cases two regions of the Tafel plot were apparent but this was not necessarily linked with the water content or purity of the electrolyte. Where only one linear portion was present the Tafel slope was approximately $(100 \text{ mV})^{-1}$.

6.1.2 Experimental and Results

The cell for the experiments reported here was similar to that used for the galvanostatic experiments except that either a platinum wire or disc in a PTFE holder was used. Experiments were carried out in both industrial electrolyte and purified electrolyte (preparation described elsewhere).

Figure 6.1 shows a typical cyclic voltammogram between +2.2 V and -0.28 V versus Pd/H₂ of platinum in industrial KF.2HF recorded at 0.1 Vs⁻¹. There are two oxidation peaks (B and C) on the forward sweep followed by a single reduction peak (A) on the reverse scan.



Figure 6.1Voltammogram of platinum in industrial KF.2HF.Sweep speed = 0.10 Vs^{-1} . Potential limits: +2.20 V \rightarrow -0.28 V.

Other slight peaks may be attributed to the presence of impurities. The cathodic branch of the voltammogram shows the evolution of hydrogen. Figure 6.2 shows a voltammogram between +2.2 V and -0.31 V in which a large oxidation peak (D) appears on reversal of the potential at the cathodic limit. This indicates a highly reversible process, probably desorption of atomic hydrogen. Figure 6.3 shows a voltammogram between +2.2 V and -0.37 V versus Pd/H₂. A new large oxidation peak (E) is seen at a potential about 0.7 V more positive than the desorption peak in Figure 6.2 and a broad bulge appears where the peak previously attributed to desorption was. It was also noted that the peak current was very much greater.

Figures 6.4 to 6.9 shows how the shape of peak E alters with sweep speed. As sweep speed increases two peaks at more negative potentials emerge, the peak height of these two increasing with sweep speed. Figure 6.10 shows the variation of peak current with sweep speed for the three peaks and peak A.

Similar voltammograms for the fluorine evolution branch were obtained in purified electrolyte. Figure 6.11 shows a typical voltammogram between the limits +2.43 V and +0.63 V at 100 mVs⁻¹. The first oxidation peak (C) is much clearer, while a single reduction peak is again seen. All three peak currents increase linearly with sweep speed (Figure 6.12).

Extending the cathodic limit to 0 V allows a second reduction peak (F) to be observed, figure 6.13. Reducing the anodic limit to +1.85 V causes this peak to be eliminated, Figure 6.14. The variation of the height of both peaks with anodic sweep limit is shown in figures 6.15 and 6.16. This shows a linear relationship apart from a discontinuity in the line for peak F at the potential limit equivalent to the potential where B occurs. The peak current of F was also found to vary linearly with sweep speed.

On extending the sweep slightly into hydrogen evolution the highly reversible oxidation peak was again observed, (Figure 6.17). However, on further extending the cathodic limit the peak did not shift completely to a more positive potential but broadened considerably, (Figures 6.18 and 6.19). The change in peak shape with sweep speed was also different from that obtained in industrial electrolyte. The one broad peak did not resolve into separate peaks but simply became narrower and the peak potential moved to a more negative value.

Steady-state current-potential data were obtained for both the anodic and cathodic branches in purified electrolyte. The data for fluorine evolution are shown in Figure 6.20 in the form of a log i-E

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As Figure 6.1, except Potential limits : $+2.20 \text{ V} \rightarrow -0.31 \text{ V}.$





As Figure 6.3, except Potential limits : $+2.20 \text{ V} \rightarrow -0.37 \text{ V}$.





As Figure 6.3, except

Sweep speed = 0.20 Vs^{-1} .



Figure 6.5

As Figure 6.3, except Sweep speed = 0.30 Vs^{-1} .





As Figure 6.3, except Sweep speed = 0.40 Vs^{-1} .





As Figure 6.3, except Sweep speed = 0.50 Vs⁻¹.



Figure 6.8

As Figure 6.3, except Sweep speed = 0.60 Vs^{-1} .



Figure 6.9

As Figure 6.3, except Sweep speed = 0.70 Vs⁻¹.



Figure 6.10 Variation in peak current with sweep speed for peaks A, D, E and G (industrial electrolyte).



Figure 6.11Voltammogram of platinum in purified electrolyte.Sweep speed = 0.10 Vs^{-1} . Potential limits : +2.43 V \rightarrow +0.63 V.



Figure 6.12 Variation in peak current with sweep speed for peaks A, B and C (purified electrolyte).



Figure 6.13Voltammogram of platinum in purified electrolyte.Sweep speed = $0.10 \ Vs^{-1}$. Potential limits : +2.43 V \rightarrow 0 V.



Figure 6.14Voltammogram of platinum in purified electrolyte.Sweep speed = 0.10 Vs^{-1} . Potential limits : +1.85 V $\rightarrow 0 \text{ V}$.



Figure 6.15 Variation of peak current for peaks A and F with positive sweep limit (purified electrolyte).



Figure 6.16Variation of cyclic voltammogram with positive sweeplimit. Sweep speed = 0.10 Vs^{-1} . Negative potential limit = +0.20 V.



Figure 6.17Voltammogram of platinum in purified electrolyte.Sweep speed = 0.10 Vs^{-1} . Potential limits : +2.40 V \rightarrow -0.04 V.







Figure 6.19





Figure 6.20 Tafel plot for fluorine evolution from platinum in purified KF.2HF.

plot. The potentials are quoted against the Pd/H_2 electrode, as elsewhere. The Tafel slope of the linear portion is $(420 \text{ mV})^{-1}$. Figure 6.21 shows the data for hydrogen evolution also in the form of a log i-E plot. The Tafel slope of the linear portion was $(50 \text{ mV})^{-1}$.

6.1.3 Discussion

In this particular study the exact values of peak potentials were not found to be reproducible. However, the whole of the voltammograms were shifted, peaks retaining the same potentials relative to each other. In each case the reduction peak A coincided with the open circuit potential. The variation in potentials relative to Pd/H_2 may be caused by the corrosion of the platinium at open circuit. Furthermore, although reference electrodes were charged in the melts where they were to be used, contamination of the paladium may be carried over from an industrial melt to a purified melt. Certainly, a Pd/H_2 electrode prepared in an industrial melt acquires a black colouration while one prepared in a purified melt does not.

It is clear that, prior to the actual fluorine evolution reaction, two surface processes occur. This is indicated by the linear relationship between peak current density and sweep speed. The two oxiation processes are probably initial fluorination process and the subsequent multilayer fluorination process as reported by Doughty et al [77]. However, the behaviour observed in purified KF.2HF differs by the presence of a second reduction peak, which was not reported in the study in HF. The process only occurs on the reverse sweep if the potential has been positive enough for the second oxidation process to occur. Therefore, if the second oxidation peak is attributed to multilayer fluorination of the platinum, it is probable that the multilayers are formed beneath the initial fluoride layer, thus making its reduction process less thermodynamically favoured. The process continues to proceed, even when its product is not removed from the electrode (Figure 6.12) and may be considered a corrosion process. To allow the continued ingress of the electrolyte to a fresh platinum surface, the fluoride layers must be imperfectly formed.

The absence of the second reduction process in industrial electrolyte must be attributed in some way to the higher levels of impurities. With the limited information available it is possible only to suggest that the deposition of metallic impurities is more kinetically favoured than the reduction of the supposed corrosion layer.

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Figure 6.21 Tafel plot for hydrogen evolution from platinum in purified KF.2HF.

Differences are also apparent between purified and industrial electrolytes for the hydrogen evolution reaction. These concern the peaks observed on the return sweep from hydrogen evolution. With industrial electrolyte there is a sudden change over from a hydrogen atom desorption peak to a peak at a more positive potential. As sweep speed is increased there is a shift back to the more negative peak. This implies that once a certain potential has been reached in the negative direction no adsorbed hydrogen atoms are present on the electrode surface, being consumed immediately they are produced. Peak E is then probably caused by the oxidation of any hydrogen gas still in the vicinity of the electrode. The large positive shift is probably caused by the deposited impurities decreasing the activity of the platinum surface. With purified electrolyte there is no sudden shift in peak position, merely a broadening of the peak and then a shift back to the more negative potential as sweep speed is increased. This reflects the much lower levels of impurities, thus allowing the proposed oxidation of molecular hydrogen to occur at a less positive potential.

6.2 Mild Steel in KF.2HF

6.2.1 Results

Figure 6.22 shows a cyclic voltammogram of mild steel in the potential range -0.22 V to +4.50 V. Two very broad oxidation peaks are seen on the forward sweep but there are no corresponding reduction peaks on the reverse scan. There is, however, another shallow oxidation peak indicating that the process (probably fluorination) was not completed on the forward sweep. Two other oxidation peaks are also seen which may be connected with the presence of metallic impurities in the melt. In the case where the anodic sweep is reversed before reaching the second oxidation peak, the first oxidation peak on the reverse scan is greatly enhanced, (Figure 6.23).

The behaviour for the hydrogen evolution branch is similar to that reported previously for a larger electrode. Figures 6.24, 6.25 and 6.26 show the effect on the voltammogram, with a sweep speed of 10 mVs^{-1} , of shifting the negative limit further into hydrogen. At the more extreme limits a nucleation loop develops and the slope of the current/potential line decreases above a potential of -1.10 V, which corresponds to a current density of 130 mAcm⁻². At the slower sweep speed of 1 mVs⁻¹ the effect is more marked, (Figure 6.27). A







Figure 6.23Voltammogram of mild steel in industrial electrolyte.Sweep speed = 0.1 Vs^{-1} . Potential limits : +2.0 V \rightarrow -0.22 V.





E / mV


Figure 6.26Voltammogram of mild steel in industrial electrolyte.Sweep speed = 0.1 Vs^{-1} . Potential limits : $0 \text{ V} \rightarrow -1.45 \text{ V}$



Sweep speed = 0.001 Vs⁻¹. Potential limits : 0 V \rightarrow -1.10 V.

maximum is seen at -1.00 V, corresponding to a current density of 86 mAcm^{-2} .

Experiments were also performed in purified electrolyte, the preparation of which is described elsewhere. Voltammograms in fresh purified electrolyte do not show the peaks observed in industrial electrolyte except at the slowest sweep speed of 1 mVs⁻¹, (Figures 6.28 and 6.29). However, in time a peak at -0.280 V developed, suggesting that the mild steel electrode was contaminating the electrolyte and that this peak might well be caused by the presence of iron.

Upon addition of PbF_2 to give a concentration of lead of 200 ppm (i.e. similar to that found in industrial electrolyte) a second peak was observed at a potential of -0.185 V, Figure 6.30, indicating that this peak is undoubtedly caused by the reduction of lead in solution and its subsequent oxidation. The addition of FeF₃ caused little change in the recorded voltammogram although there may be some enhancement of the more cathodic peak if the electrode is held in hydrogen evolution for a given time and then the potential scanned in the anodic direction, -(Figures 6.31 and 6.32).

Steady-state data were obtained for hydrogen evolution in purified electrolyte at low current (to exclude bubble effects). These are shown in the form of log I versus E plot in Figure 6.33. The Tafel slope was found to be $(100 \text{ mV})^{-1}$.

6.2.2 Discussion

Mild steel is seen to corrode faster than platinum, and the process seems to be irreversible as no reduction peaks are apparent. The more anodic peak represents a second fluorination process which prevents the continuation of the first. The small iron oxidation peak seen previously at a more negative potential is probably due to the removal of the dendritic deposit on the surface of the electrode. The broad peaks at more positive potentials must then be caused by the corrosion of the actual mild steel in order to account for the large amounts of charge associated with the processes. The latter observation and the absence of a reduction peak implies that the first iron species (probably Fe²⁺) is removed into solution, while the second iron species (probably Fe³⁺) passivates the electrode with regard to further oxidation. The two oxidation peaks on the return sweep are due to the fluorination of solution species of iron and lead, which now proceeds because of the presence of fluorine gas (i.e. $Fe^{2^+} \rightarrow Fe^{3^+}$ and $Pb^{2^+} \rightarrow Pb^{4^+}$).



Figure 6.28Voltammogram of mild steel in purified electrolyte.Sweep speed = 0.1 Vs^{-1} . Potential limits = $0 \text{ V} \rightarrow -0.80 \text{ V}$.





Figure 6.31Voltammogram of mild steel in purified electrolyte +200 ppm Pb.Sweep speed = 0.1 Vs^{-1} . Potential limits : +0.07 V \Rightarrow -0.8 V.



Figure 6.32 Voltammogram of mild steel in purified electrolyte + 200 ppm Pb + 400 ppm Fe. Sweep speed = 0.1 Vs⁻¹. Potential limits : +0.07 V \rightarrow -0.8 V.





Figure 6.33 Tafel plot for hydrogen evolution from mild steel in purified KF.2HF.

Little information can be obtained about the mechanism of hydrogen evolution, which would require more exhaustive experiments. However, some insight may be gained into the potentials at which iron and lead species are reduced. There is a complete absence of reduction peaks in the voltammograms obtained, apart from the case where the potential is reversed immediately after a stripping peak, when the metallic species is still in the vicinity of the cathode. The concentrations of iron and lead species are sufficiently low for their reduction to be controlled by mass transport. The loops observed in figures 6.25 and 6.26 are reminiscent of those seen for nucleation processes, although the charge they contain seems rather large. However, no such loop is seen in figure 6.24 and only one oxidation peak, which can now be associated with lead. Figure 6.25 shows two oxidation peaks, implying that both iron and lead can now be deposited. The decrease in the current/potential slope in figure 6.26 is attributed to the shielding effect of bubbles. A more extreme situation is shown in figure 6.27 where a slower sweep speed is used where current actually decreases.

From these observations it is concluded that lead is probably deposited on the electrode before iron, which agrees with the relative positions of their oxidation peaks. This also concurs with observations of the form of the deposit. Lead deposits directly onto the mild steel in a firmly held layer and it is on this that the mossy dendritic deposit of iron and probably more lead accumulate .

CHAPTER 7

EXPERIMENTAL DETERMINATION OF OHMIC POTENTIAL DROP

7.1 Introduction

The quantification of ohmic drop components caused by the presence of bubbles in the inter-electrode gap has been attempted by a number of workers.

Janssen and Barendrecht [54] determined the ohmic resistance of a thin solution layer at a gas evolving electrode by the alternating current impedance method. The ohmic resistance is obtained from complex plane plots. The real component of the impedance, z', is plotted versus the imaginary component of impedance, z", at various frequencies. The intersection of the z"/z' curve with the z' axis at $\omega \rightarrow \infty$ denotes the ohmic resistance of the cells, R. R₀ is obtained by determining R at i = 0 and various frequencies and/or extrapolation of the R/i curve. The bubble effect upon the resistance R is given by the reduced resistance increase $\Delta R^* = (R-R_0)/R_0$.

An alternative method of determining the ohmic potential drop is by the current-interruption technique. The immediate drop in working electrode potential on interruption of the current is separated from the more gradual decay due to the discharge of the double layer.

By use of the current interruption technique Janssen et al [55] obtained a dimensionless correlation for the increase in ohmic resistance due to the presence of gas bubbles. The system used was that for alkaline water electrolysis with electrodes of various geometries: expanded nickel gauze, nickel in a Venetian blind type electrode and a nickel electrode of zig-zag type. The effect of a range of parameters was determined: current density, solution flow rate, distance between diaphragm and working electrode, distance from rear of the working electrode to the back of the working electrode compartment, the height of the electrolysis cell, the electrode type, nature of the electrode surface and of the gas evolved. They reported the interesting result that ΔR^*_{WM} (the reduced resistance of the solution layer with presence of bubbles between diaphragm and working electrode) was independent of current density in the current range investigated.

However, in a later alternating current impedance study [54] on small (0.5-4 mm) planar working electrodes the relationship $\log \Delta R^* = a$, + b log i was found to apply for hydrogen evolving electrodes, where b does not depend on the diameter, position and material of the electrode, pressure and temperature but does significantly depend on concentration of KOH solution. The factor a, depends on the position, height and material of electrode, temperature and KOH concentration.

Kuhn and Stevenson [53] reported current-potential measurements at a gas evolving anode and cathode in sulphuric acid. The effect of Luggin capillary diameter and its distance from the working electrode is given. Except at the highest current densities the offset distance was not too critical and the shielding due to the Luggin seemed unimportant, which was ascribed to the fact that shielding effects were already operative due to the presence of bubbles. However, they do stress that the technique of current interruption is often mis-used, most commonly by basing readings on too slow a reading speed (e.g. oscilloscope sweep rate). This results in the instantaneous voltage drop, which represents the ohmic factor, being followed asymptotically by the capacitive decay. Under these circumstances separation of the two components is impossible. Early oscilloscopes were, in many cases, not sufficiently fast and results obtained from them should be treated with caution. Janssen et al [55] investigated the effect of the time base on the experimental ohmic potential drop as it is known that this is influenced by recording speed. Their results showed that, while the $\Delta V'$ versus i plots for two different time bases will have the same slope, they intersect the $\Delta V'$ axis at i = 0 at different values of $\Delta V'$, denoted $\Delta V''$. Therefore it is necessary to use the same time base throughout so results may be compared. The effect should be taken into account when calculating the ohmic resistance R of the gas bubble containing solution layer. Thus, $\Delta V = \Delta V' - \Delta V''$ and $R = \Delta V/i$.

Another limitation to the technique is described by LeRoy et al [78] in that its use should be restricted to cells where the total current is less than IA because of inductive effects with larger currents.

Gallone et al [58] obtained anodic and cathodic polarisation curves in the temperature range 40-80°C in 30% KOH with the Luggin in two positions - inserted from behind so as to be at exactly zero distance from the electrode working surface or in front of the electrode, 3 mm from the working surface. However, they discovered that, after deduction of the ohmic terms, the two Tafel plots were nearly coincident, thus showing the reliability of the method.

7.2 Experimental

The cell used was of a design described earlier where the working electrode was a metal disc (mild steel or nickel) in a PTFE holder in a vertical orientation. The electrolysis current was supplied by a Thomson Ministat (0-20 V, 0-15A). Bounceless switching was achieved by an R.S. components mercury-wetted relay (operated by a 5 V power supply) inserted in the counter electrode lead. Transients were recorded using an oscilloscope (Gould, Digital storage oscilloscope, OS4000) and output to an X-Y chart recorder (Bryans 26000). A buffer amplifier (Fylde 351UA) was inserted between potentiostat and oscilloscope.

The experimental procedure was fairly simple. The required current density was set on the potentiostat (acting as a galvanostat) and the circuit closed for the electrode to evolve hydrogen. After the desired period of operation the power supply to the mercury-wetted relay was turned off and the circuit broken. The oscilloscope was triggered by the falling voltage. The crude Luggin probe was positioned about 2 cm away from the working electrode to prevent bubbles blocking the pathway. This was similar to the distance used by Janssen and Barendrecht [54] in their current interruption experiments to check the results obtained by the alternating current impedance method.

7.3 Results

A typical voltage transient is shown in figure 7.2. Very sharp switching was achieved with the mercury-wetted relay. In comparison Janssen et al [55], who used a mechanical switch, recorded oscillations of potential after operating the switch and had a switching time of about 15 ms. They however generally had different time bases before and after switching. In these experiments the same time base was maintained throughout the transient.

The effect of time base was investigated. Figure 7.3 shows the ohmic potential drop, $\Delta E'$, as a function of current density for three time bases. At faster time bases the triggering of the oscilloscope was less reliable, often "missing" the transient. All the lines show the same slope but intersect the $\Delta E'$ axis at i= 0 at different values of ΔE_0 . In general a time base of 10 ms cm⁻¹ was used which gave consistent and reliable triggering. In addition each set of results was corrected by subtracting the apparent ohmic potential from $\Delta E'$, i.e. $\Delta E = \Delta E' - \Delta E_0$.



A -Carbon anode BA-Buffer amplifier C-Mild steel cathode CR-X-Y chart recorder CRO-Storage oscilloscope DVM-Digital volt meter POT-Potentiostat R-Reference electrode S-Mercury-wetted relay / switch Yt-Yt recorder

Figure 7.1 Diagram of circuit for measurement of ohmic potential drop.









Figure 7.4 shows ohmic potential drop, AE, at nickel and mild steel electrodes versus current density for a complete range of the latter at run times of 10 s. The bubbles formed at a mild steel electrode are small spherical, freely evolved and spread approximately 0.5 cm into the electrolyte. In contrast the bubbles produced on nickel are extremely lenticular, not freely evolved and do not spread into the electrolyte, skimming up the electrode surface. The differing bubble characteristics are highlighted by the AE values for nickel being very much larger than those for mild steel. A linear relationship between ΔE and i is seen throughout the current density range used for the mild steel electrode (0.040-0.600 Acm⁻²), with an increase in specific resistance ($\Delta E/i$) of 0.89 Ωcm^2 . The current density range for the nickel electrode included values down to 0.005 Acm⁻². In the range 0.10-0.60 Acm⁻² the increase in specific resistance was found to be 1.30 Ω cm². At the lower current densities the slope of the $\Delta E/i$ plot was steeper. This implies that the specific resistance in the range 0.005-0.10 Acm⁻² is greater than at higher current densities.

Figure 7.5 shows a ΔE vs i plot for hydrogen evolution at a mild steel electrode after 30 minutes of operation. In this case large bubbles developed at higher current densities and these were not freely released into the electrolyte. In the current density range 0.10-0.40 Acm^{-2} the increase in specific resistance was found to be 2.04 Ωcm^2 . At the lower current densities a higher increase in specific resistance was apparent as in the experiments with a nickel electrode.

Also shown in figure 7.5 are the values of the working electrode potential after 30 minutes (E_{final}). Figure 7.6 shows a Tafel plot using these uncorrected data. It can be seen that the relationship does not hold when areas of the electrode are obscurred by gas bubbles. Using the corrected data, $E_{final} - \Delta E$, resulted in the plot shown in figure 7.7 which has a Tafel slope of (90 mV)⁻¹.

A limited number of ΔE measurements were made for hydrogen evolution at a nickel electrode after 30 minutes of operation. These are shown in figure 7.8. The values of ΔE are similar to those for mild steel after a 30 minute period of electrolysis and lower than for nickel after 10 seconds of operation. There is a linear relationship between ΔE and current density in the current density range 0.05 to 0.30 Acm⁻².

In general the results within each set of experiments show good correlation. However, the ΔE determinations are susceptible to the

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<u>Figure 7.4</u> Ohmic potential drop/current density plots for mild steel and nickel. t = 10 s.



<u>Figure 7.5</u> Ohmic potential drop and final operating voltage versus current density for mild steel. t = 30 mins.



Figure 7.6 Tafel plot (uncorrected) for hydrogen evolution on "mild steel".



Figure 7.7 Tafel plot (corrected) for hydrogen evolution on "mild steel".



Figure 7.8 Ohmic potential drop versus current density for nickel. t = 30 mins.

condition of the electrolyte. This was shown by determining ΔE after 30 minutes in electrolyte which had been depleted of HF. It was found that atcurrent densities of 0.40 Acm⁻² and higher polarisation occurred. The values of ΔV obtained at lower current densities were approximately 50% greater than for new electrolyte, figure 7.9. Therefore, to allow comparison of the results for different materials and times of operation it was essential to use fresh electrolyte for each set of experiments.

7.4 Discussion

In order to account for the lack of variation of specific ohmic resistance with current density observed in a variety of studies, it has been proposed that virtually all ohmic resistance is located in a layer at the electrode surface. This view is supported by the observation that there is no difference in the resistance of the working-reference gap for an electrolyte whether bubble filled or devoid of bubbles [53]. Therefore either the contribution from bubbles in the bulk is of minor importance or the bubbles rise faster at greater current densities so that the void fraction does not change in proportion with current density.

Experiments with mild steel over 30 minutes and with nickel over 10 seconds show that the increase in specific resistance is constant at current densities higher than about 0.10 Acm⁻². One of the main differences between operation of mild steel for 30 minutes at high and low current densities would seem to be that bubbles are more likely to be released into the electrolyte at low current densities. This might suggest that there is an appreciable contribution from bubbles in the bulk which is lessened as the bubbles adhere more to the surface, especially as gas evolved in small bubbles will cause a larger void fraction than gas in larger bubbles. However, this does not apply in the case of nickel, which evolves large, lenticular bubbles throughout the current density range used and would contradict the evidence presented by other workers. Furthermore, the efficiency of gas evolution is decreased at lower current densities [79], (i.e. a smaller proportion of the gas generated in dissolved form is transformed into the gaseous phase of bubbles). In the case of nickel, there is photographic evidence that larger bubbles persist for longer at low current densities than at higher current densities.

The other important factor is the change in the electrode surface occasioned by the deposition of metallic impurities. In a previous



<u>Figure 7.9</u> Ohmic potential drop versus current density for mild steel-depleted electrolyte. t = 30 mins.

chapter it was concluded that it is quite possible that the deposited material becomes the active surface for hydrogen evolution which has a levelling effect on the performance of differing electrode materials. It would appear that this deposit either masks the nucleation sites on mild steel and/or has few nucleation sites itself. In the case of nickel the number of nucleation sites seems to increase when the deposit is present, implying that the active nucleation sites are located on this layer.

The decreased specific resistance at higher is probably linked with an increase in available surface area. The current densities quoted are nominal and do not include the effects of the deposit. Therefore, the slope of the ΔE /current density plot should be greater than portrayed. Nickel shows a higher initial operating potential caused by the larger ohmic drop, which will mean a faster rate of deposition than for mild steel. This is why mild steel shows uniform behaviour throughout the current density range at short times and nickel does not. This also explains the changing slopes. At low overvoltages either no impurities are reduced or perhaps only one, probably lead. Once a certain overvoltage is exceeded the surface area is increased and a change in bubble characteristics occurs. Again the deposit has a levelling effect, in this case, on ohmic potential drop. This is confirmed by the specific resistance of nickel after 30 minutes being similar to that of mild steel after the same period of time.

In conclusion, the results are in agreement with a theory that a gas film exists and that the resistive component is mainly located here. The bubbles attached to the surface are a part of this film. The presence of large bubbles on nickel indirectly catalyses the formation of a dendritic deposit of a large surface area, thus allowing smaller bubbles to be formed. A similar effect probably also acts on mild steel, initially causing a large increase in ohmic component but eventually moderating it.

CHAPTER 8

PHOTOGRAPHIC STUDY OF HYDROGEN EVOLUTION

8.1 Photographic Equipment

A Pentax ME Super camera with a standard 50 mm lens was used. This system was modified with a 12 mm extension tube and a +4 diopter lens attachment. The film used was black and white 400 ASA XP1 (Ilford) developed with a standard C41 process. The cell was illuminated from the rear by a 15 W light source, and observed through the glass window in the front face of the heater unit.

8.2 Photographic Study of Hydrogen Evolution on Mild Steel

The electrode was of a spade type, dimensions 30 mm x 25 mm, cut from a thin mild steel plate and positioned centrally in the cell, face on to the counter electrodes. The electrolysis current was provided as previously.

Figures 8.1 to 8.5 show how the gas bubbles increase in size over a 45 minute period from the start of electrolysis at a current density of 0.04 Acm⁻². Figures 8.1 and 8.2 are both at 7 minutes but taken at different angles. Gas can be seen streaming upwards from the top of the electrode and it can be seen that bubbles do not spread into the electrolyte. Figure 8.3 shows that after 16 minutes of electrolysis gas is still streaming from the top of the electrode, but also that larger bubbles are developing. Figures 8.4 and 8.5, taken at 35 and 43 minutes respectively, show the established bubble layer with bubble diameters of up to 2 mm and contact angles of approximately 90°. The potential-time profile is shown in figure 8.6 with the time of each photograph marked.

8.3 Photographic Study of Hydrogen Evolution on Nickel

The electrode was of a similar size and shape to that used above, cut from nickel foil.

Nickel had previously been observed to evolve larger bubbles than mild steel and this is shown in the photographs obtained. Figure 8.7 and 8.8 show hydrogen evolution at the nickel electrode at a current

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Figure 8.1 Hydrogen evolution at mild steel. Current density = 40 mAcm^{-2} . t = 7 mins. Magnification x 3.6.



Figure 8.2 As Figure 8.1



Figure 8.3 As Figure 8.1, except t = 16 mins.



Figure 8.4 As Figure 8.1, except t = 35 mins.



Figure 8.5 As Figure 8.1, except t = 43 mins.



Figure 8.6 Potential/time profile for hydrogen evolution at mild steel. $I = 40 \text{ mAcm}^{-2}$.



Figure 8.7 Hydrogen evolution at nickel. $I = 40 \text{ mAcm}^{-2}$. t = 5 mins. Magnification x 3.6.



Figure 8.8 As Figure 8.7, except t = 8 mins.

density of 0.04 Acm⁻². They correspond to 5 minutes and 8 minutes after the start of electrolysis respectively. The relevant potentialtime profile is shown in figure 8.9. After 5 minutes of operation bubbles with diameters of up to 2.5 mm were seen, which were distorted by buoyancy forces tending to lift the gas bubble upwards from the point of attachment. After a further 3 minutes the bubble characteristics had changed, the diameters being smaller and the shape less distorted. Furthermore, figure 8.8 shows that bubbles are released from the electrode into the electrolyte rather than skimming up the surface.

Another point of interest is illustrated by figure 8.10, which shows an electrode operating at a current density of 0.02 Acm^{-2} , after 8 minutes electrolysis. The gas bubbles are very lenticular, with contact angles of over 90°. They are also distorted and have diameters of up to 3 mm. These bubbles are, in fact, larger than those observed at the higher current density of 0.04 Acm^{-2} .

8.4 Photographic Study of Parallel Strand Expanded Metal Electrodes

8.4.1 Introduction

Expanded metal electrodes are characterised by various parameters as illustrated in figure 8.11. The long way dimension is precise and constant, while the short way dimension is approximate. Sheet size is given conventionally with the long way dimension first. A further characterising parameter is the percentage open area for which two figures are given; at normal incidence, when the sheet is viewed while held at right angles to the line of vision, and at maximum incidence, when the sheet is viewed in a slanted position, so that the thickness of the strands is parallel to the line of vision, thus presenting a greater open area. This latter parameter applies only to unflattened meshes.

8.4.2 Experimental

A range of samples of mild steel meshes were obtained from "The Expanded Metal Company". When received these were coated in a protective layer of lacquer, which was removed by soaking in warm trichloroethylene and 50% HC1.

For the purpose of this study it was decided that the parallel strand type would be most effective and of these the two with the largest percentage open area were chosen. These were the 401 and 402 meshes, the parameters of which are given below:

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a fig. 8.7 b fig. 8.8

Figure 8.9 Potential/time profile for hydrogen evolution at nickel. I = 40 mAcm⁻².



<u>Figure 8.10</u> Hydrogen evolution at nickel. $I = 20 \text{ mAcm}^{-2}$. t = 8 mins. Magnification x 3.6.
Figure 8.11 Diagram showing parameters for classification of expanded metals.



CONVENTIONAL EXPANDED MESHES

Figure 8.11 Diagram showing parameters for classification of expanded metals.

CONVENTIONAL EXPANDED MESHES





MESH	LW	% OPEN AREA		WIDTH	THICKNESS	WEIGHT
	mm	NOR	MAX	mm	mm	kgm ⁻²
401	28.575	42	64	2.311	0.75	3.672
402	28.575	43	67	2.667	0.75	3.707

Examples of the 401 and 402 meshes are shown in figure 8.12. The dimensions of the electrodes used were 47 mm x 35 mm and electrical contact was made by a copper strip. The electrodes were suspended from the PTFE electrode assembly/lid and oriented so that gas would be removed upwards and to the rear of the electrode.

8.4.3 Results

Figures 8.13, 8.14 and 8.15 show a 401 mesh electrode operating at a nominal current density of 0.04 Acm^{-2} at times after start of electrolysis of 200 seconds, 150 seconds and 180 seconds respectively. These show that there is a build up of bubbles over a fairly short period of time. Misting of the electrolyte occurs rapidly which had not been observed when using planar electrodes. Figure 8.15 also shows evidence of material of a particulate nature circulating in the electrolyte to the rear of the electrode.

Figure 8.16 shows a side view of a 402 mesh electrode in the electrolyte. This mesh has a slightly higher percentage open area, in both orientations, than the 401 mesh. Figures 8.17, 8.18 and 8.19 show a 402 mesh electrode operating at a nominal current density of 40 mAcm⁻². Rapid misting of the electrolyte occurred within 3 minutes (Figure 8.18), but cleared slightly after a longer period of operation (Figure 8.19).

8.4.4 Discussion

Severe clouding of the electrolyte prevented detailed observation of the bubble evolution from the parallel strand electrodes. This is probably caused by a fine dispersion of gas in the electrolyte or, alternatively, by particles circulating in the electrolyte. With regard to the latter proposition, the electrolyte seemed to be circulated much more by the release of gas than in the case of a simple planar electrode. Particles may either be swept up from the bottom of the cell or removed from the electrode deposit by the scouring action of the gas. Indeed, when the electrode was examined after use no dendritic deposit was apparent. This may be an advantage as, otherwise, the apertures in the mesh might become blocked. Furthermore, if



(a) 401 mesh O:7 x actual size



(b) 402 mesh O.7 x actual size

Figure 8.12



Figure 8.13 Hydrogen evolution at mild steel 401 mesh. Nominal I = 40 mAcm⁻². t = 2 mins. $3.8 \times$ magnification



Figure 8.14 As Figure 8.13, except t = 2.5 mins. 3.8x magnification

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Figure 8.15 As Figure 8.14, except t = 3 mins. $4 \times magnification$



Figure 8.16 Side view of 402 mesh in electrolyte. 3.8 × magnification



FACE

Figure 8.17 Hydrogen evolution at mild steel 402 mesh. Nominal I = 40 mAcm⁻². t = 2 mins. $3.8 \times$ magnification



Figure 8.18 As Figure 8.17, except t = 3 mins. 3-6 × magnification



Figure 8.19 As Figure 8.17, except t = 45 mins. Hx magnification

the mild steel remains clear of the deposit the smaller size of bubble may persist throughout electrolysis.

With regard to the deflection properties of the meshes, it appeared that more gas bubbles were present behind the working face than in front. However, a large amount of gas was circulating in the interelectrode gap. Unfortunately, the time available for this particular study was limited and much further work is needed to optimise the arrangement. In practice it may be possible to operate at a lower nominal current density than 0.04 Acm^{-2} and thus increase the percentage deflection of the gas bubbles.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1 Conclusions

It has become apparent, during the course of this study, that the actual material of fabrication of the cathode has, overall, little influence on the final working overvoltage. This is because of the high level of impurities in the industrially used electrolyte, which deposits onto the cathode during hydrogen evolution and becomes the active surface for this reaction. The effect of the deposit is not necessarily detrimental. In fact, mild steel is the only cathode material studied where a beneficial effect was not observed. Lead, while not producing excessively large bubbles, has a decreased overvoltage after a short period of operation. This is due to the greater activity of deposited iron over the lead substrate and an increase in surface area. Mild steel in an unmodified state seems to have very good bubble evolution characteristics. However the deposition of impurities causes an increase in contact angle and bubble size. It was also seen that electrodes with high catalytic activity, i.e. platinised mild steel, are adversely affected by the deposit which masks the active sites as well as impairing bubble release.

The beneficial effect of the deposit on the bubble releasing properties of nickel was shown by the measurement of ohmic potential drop in conjunction with visual observations. The ohmic potential drop at the start of electrolysis at a nickel electrode is significantly greater than after 30 minutes of operation. When combined with the observation that bubble diameters of 3 mm can be seen at the start of electrolysis, giving way to much smaller bubbles after a fairly short period of time, it was concluded that the desired bubble characteristics are a small contact angle, small diameter and a spherical shape. With a mild steel electrode bubbles were freely evolved initially but increased in size with time and a corresponding increase in ohmic potential drop was seen. Therefore, it is concluded that, while such high levels of impurities are present in the electrolyte, the best material for fabrication of cathodes is one which is durable, structurally useful and cheap. As it is not cost effective to purify industrial electrolyte and mild steel has superior bubble release characteristics at the start of electrolysis, the choice of cathode material is certain to remain the same. Consequently any gains in energy saving will have to be as a result of reduced ohmic losses either by reducing the interelectrode gap or decreasing the gas film on an electrode.

On the limited information gained in this study it would seem that parallel strand meshes do, to some extent, deflect hydrogen gas to the rear of the electrode. If this is so, then anodes and cathodes may be moved closer, decreasing the ohmic component from the electrolyte. There is also the possibility that the action of the gas clears the electrode of any dendritic deposit, thus allowing smaller bubble sizes to predominate and reducing the ohmic component due to the gas film.

9.2 Suggestions For Future Work

(1) More extensive experiments in purified electrolyte could elucidate further the mechanisms operating on platinum and mild steel electrodes.

(2) Confirmatory work, again in purified electrolyte, to show the effect of impurities or their absence on bubble characteristics on mild steel and nickel, i.e. would their initial bubble types remain constant throughout operation.

(3) A thorough investigation of expanded metals, possibly including quantification of ohmic components.

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