Optimisation of anode characteristics of calcium thionyl chloride cells

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Optimisation of Anode

Characteristics of Calcium

Thionyl Chloride cells

by

Jonathan Bradley

Supervisor: Dr. P.J. Mitchell

Industrial Supervisor: Dr. C.D.S. Tuck.

A Doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology, (April 1991)

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But Scientists who ought to know,
Assure us that it must be so ...
Oh! let us never, never doubt
What nobody is sure about.

Hilaire Belloc
(1870 - 1953)
The original work described in this thesis is my own except as specified in acknowledgements or footnotes and has not been submitted in full or in part, to this or any other institution for a higher degree.
Synopsis

In the field of high performance primary battery systems lithium anoded cells have been shown to have an excellent performance and extremely good shelf life. The major drawback with the lithium technology is one of safety, whereby abuse conditions (such as charging of the cell) lead to an unstable system with the very real possibility of a cell explosion. For a commercially available cell consideration of safety issues would preclude the marketing of a high performance lithium cell for general use, rather, it will be reserved for specialist e.g. Military, use where the personnel having contact with the power source can be trained in it's safe operation.

The work described in this thesis is concerned with the development of a high performance battery system utilising calcium as the anode material. Calcium has received attention as an anode material for a high performance battery system because it removes many of the safety problems associated with lithium. The major disadvantages of calcium have been addressed namely the shelf life and discharge performance. The electrochemical techniques of cyclic voltammetry and a.c. impedance have been used in conjunction with physical methods such as scanning electron microscopy to define the mode of operation of these cells.
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List of Symbols

Cd  Diffusional Capacitance
Cdl  Double Layer Capacitance
E  Theoretical E.M.F.
i  Current
icorr  Corrosion Current Density
Imax  Amplitude of Alternating Current
j  Complex Number ( /-1 )
R  Resistance
Rd  Diffusional Resistance
Re  Electronic Resistance
Ri  Ionic Resistance of S.E.I. Film
Rn  Solution Resistance
ti  Transport Number
V  Open Circuit Voltage
Vmax  Amplitude of Alternating Voltage
V/V  Volume / Volume Percentage Solution
W  Warburg Impedance
Z  Complex Cell Impedance
Z'  Real Impedance Component
Z''  Imaginary Impedance Component
|Z|  Absolute Value of Impedance
$\delta C$  Change in Concentration

$\delta X$  Change in Distance from Electrode

$\Theta$  Charge Transfer Resistance

$\phi$  Phase Angle Between Current and Voltage

$\tau$  Surface Roughness Factor

$w$  Angular Frequency
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Chapter 1

Introduction

In the field of high performance primary battery systems lithium anoded cells have been shown to have an excellent performance and extremely good shelf life. The major drawback with lithium technology is one of safety, whereby abuse conditions (such as accidental charging of the cell), lead to an unstable system with the very real possibility of a cell explosion (this is further detailed in the review, chapter 2). For a commercially available cell consideration of safety issues would preclude the marketing of a high performance lithium cell for general use, rather, it will be reserved for specialist e.g. military, use where the personnel having contact with the power source can be trained in it's safe operation.

The work described in this thesis is concerned with the development of a high performance battery system utilising calcium as the anode material. Calcium has received attention as an anode material for a high performance battery because it removes many of the safety problems associated with the lithium technology.

A number of classical electrochemical techniques have been utilised in order to compare the effect of additives on the behaviour of calcium thionyl chloride cells. The aims of this thesis have been to monitor improvements in performance of the anode and the electrolyte and the reduction of anode corrosion at open circuit.

In order to study the behaviour of anode, the
electrolyte and the corrosion effects, techniques of optical microscopy and weight loss were used. This was augmented by electrolyte solubility data, cyclic voltammetry and impedance measurements.

The behaviour of the calcium electrode on load was studied by discharge experiments, further cyclic voltammetry and impedance measurements. In every case to reinforce the electrochemical data so obtained electron micrographs were taken at appropriate stages throughout the experimental work. These studies are reported and summarised in chapter 9.

As a consequence of the work reported in this thesis novel solutions to the open circuit corrosion and the inferior discharge performance (with respect to Lithium anoded cells), have been proposed and tested. From a baseline system that was available at the start of this project improvements of circa 300% in the cells performance and over 200% in terms of the open circuit corrosion have been realised.

As a direct result of this research it is now possible to propose mechanisms for the corrosion behaviour of the anode, the effect of electrolyte solubility and the overall limitations in the performance of a calcium thionyl chloride cell. These are reported and discussed in chapter 10.
Chapter 2

Calcium Thionyl chloride cells a review

Over the past 15 years the search has continued for compact, high performance cells. This demand has been fuelled by the increase in the number of electronic devices and their consequent miniaturisation. Lithium anoded cells have an extremely good shelf life and on load performance but doubts still exist as to their safety. The principal disadvantage with a lithium cell occurs during either reversal or charging. Under these conditions so called "mossy" lithium can be deposited on to anode, cathode, or other cell components. This results in the danger of a short circuit within the cell with consequent temperature rise and the possibility of a molten anode leading to a cell explosion. Calcium as the anode material has an inherent advantage in that its melting point is much higher, (670°C above that of Lithium) thus the danger of thermal run-away has been lessened / removed. In addition it has proved to be impossible in practical terms to deposit calcium on to the anode or other cell components. This is an important safety feature in that no "mossy" calcium can be formed and the cell cannot short out under these conditions.

When either Lithium or Calcium is placed into a thionyl chloride supported electrolyte they form on contact a film
of the metal chloride. This film has the properties of a solid electrolyte, in that it is a poor electronic conductor but a rather good ionic conductor. Hence the passage of current is due to ion movement. These cells are known under the collective name of Solid Electrolyte Interphase (or SEI) batteries.

In a calcium anoded cell the SEI will be of calcium chloride, as a poor electrical conductor the passage of current will be predominantly by ionic defect sites. Peled (1) has measured the transport number of calcium for a calcium tetrachloroaluminate, thionyl chloride cell and found it to be very low, while that of chloride ions is close to unity. From his results the passage of current will be principally due to the ability of the chloride ions to pass through the calcium chloride film. In his paper he shows that the calcium cell behaves as an "electrochemical diode", in that current can pass easily in one direction but that the cell operates at a very high resistance in the reverse direction (i.e. under cathodic polarisation). Thus under anodic discharge the cell can deliver currents up to 50 mA cm\(^{-2}\) whereas under conditions of reversal or charging only a very small current is observed, (less than 0.1mA cm\(^{-2}\) up to a 30V reversal). This proves that for practical purposes it is impossible to charge a calcium , calcium tetrachloroaluminate, thionyl chloride cell. Peled (2) has proposed a mechanism to explain this phenomenon. He states that the anion of the SEI cannot get into the electrolyte
since calcium chloride is itself insoluble. When a cell is reversed the chloride ions move from the calcium anode solid electrolyte interface across the SEI to the solid electrolyte solution interface. If they were soluble the chloride ions could then diffuse away from the calcium chloride layer leaving behind lattice defects into which fresh chloride ions could move. However as the chloride ions are insoluble this migration will cease when all the available lattice defects have been filled. Consequently the charging current will also fall. When the cell is subject to anodic discharge chloride ions will move from the solution across the SEI to the calcium solid electrolyte interface. At this point there are two possibilities, one by which further migration of chloride ions into defect sites from the solution which will lead to a thickening of the SEI or alternatively where the calcium ions move from the SEI into the solution. Under these conditions the overall thickness will remain constant. In parallel with these two possible processes breakdown of the film due to corrosion and its consequent repair will also take place.

Lithium anoded cells have a completely different conduction mechanism to that for calcium. In lithium systems it is the lithium ions that cross the SEI since their transport number in lithium chloride is close to unity. Lithium chloride is the layer that forms on the lithium anode.

Peled and his co-workers (3) tried unsuccessfully to deposit calcium onto inert tungsten electrodes at current
densities up to 20 mA cm\(^{-2}\). In both reversal and charging tests there was no indication of calcium deposition.

Meitav and Peled (4) compared the safety of calcium / thionyl chloride cells using a calcium tetrachloroaluminate electrolyte to those using a lithium tetrachloroaluminate electrolyte. With a Ca(AlCl\(_4\))\(_2\) no practical current could be observed up to a charging voltage of around 40V. By contrast with a Li(AlCl\(_4\)) electrolyte the reverse voltage was measured at below 3V at a current density of 20 mA cm\(^{-2}\). They concluded that Li(AlCl\(_4\)) electrolyte was inferior to Ca(AlCl\(_4\))\(_2\) in a calcium thionyl chloride cell since the problems already observed in lithium thionyl chloride cells would be present. This would result in a double penalty in that the performance of calcium anoded cells is not as good as that for lithium, so that on load times would be reduced and the safety aspect, a major advantage of calcium anoded cells would also be lost.

Physical properties of the calcium chloride SEI film have been investigated by Meitav and Peled (5 and 6) They looked at the film thickness and also its capacitance and resistance. They concluded that the film thickness was dependent on the discharge current density of a calcium thionyl chloride cell. They measured the film resistance as ranging from 10\(^8\) ohm/cm to 10\(^{10}\) ohm/cm. Peled found (7) that the overall thickness of the SEI was greater than that predicted from interfacial measurements. The difference increased with an increased time of immersion of the calcium
anode in the cell. He concluded that the SEI is formed of two layers, one which is compact and the other more diffuse in structure. It is the compact layer that acts as the SEI and this layer is closest to the calcium anode. The second more diffuse layer is composed of reaction products and is more open in structure. This does not take part in the deposition-dissolution process and only acts as a block covering the surface of the anode. Peled also stated (2) that the resistivity of the system increased with the immersion time only at open circuit. Under load he observed a decrease in the resistivity of the film to a value similar to that of a freshly immersed electrode in to the electrolyte.

With a fresh electrode and consequently thin SEI the space charge regions will overlap (as they are situated near both interfaces). As time passes at open circuit the SEI will become thicker and these space charge regions will separate. In doing so they will include progressively less of the SEI. When an electrode is first immersed into the electrolyte the SEI will be less ordered being made up of smaller crystals. Consequently there will be a higher concentration of grain boundaries and mobile lattice defects. This will also be the case for an SEI which is being continually attacked because of anodic polarisation (whilst on load) or excessive corrosion. In these cases the SEI will be continually renewed and not allowed to grow thicker. By contrast an electrode where the SEI has been allowed to grow for example during storage will be much
thicker. The crystals of calcium chloride will be larger and have a greater degree of order with fewer lattice defects. Hence the contribution of the grain boundaries will be lessened.

Meitav and Peled (8) have cathodically polarised a calcium cell containing a lithium tetrachloroaluminate, thionyl chloride electrolyte. This resulted in lithium being deposited as soon as the charge reached 0.005mC cm\(^{-2}\). They found that about 3\% of a monolayer of lithium was required in order to stabilise a potential of 0V, measured against a lithium reference electrode. The open circuit voltage was measured at 0.7 - 0.75 V for a fresh cell. They explained this observation by saying that the calcium chloride SEI protected the lithium deposited on it from undergoing immediate fast corrosion. The resistivity of the film on the anode was initially measured at 0.4x10\(^{10}\) ohm/ cm. After the lithium had been deposited the resistivity was re-measured at 1.5x10\(^{8}\) ohm/cm. The first value is identical to that measured for a calcium/ calcium tetrachloroaluminate/ thionyl chloride cell. The second is similar to that expected for a lithium /thionyl chloride SEI.

CONDUCTIVITY OF ELECTROLYTES

Several different tetrachloroaluminate electrolytes have been tried with calcium / thionyl chloride cells. Most work has been done with LiAlCl\(_4\) and Ca(AlCl\(_4\))\(_2\). In addition recent interest has been shown with Ba(AlCl\(_4\))\(_2\) and
particularly Sr(AlCl$_4$)$_2$ (9 and 10). The method of preparation of Ca(AlCl$_4$)$_2$/SOCl$_2$ electrolyte is fairly easy and was first put forward by Staniewicz (11). It involves the initial addition of aluminium chloride to thionyl chloride, followed by calcium chloride with stirring. The mixture is then refluxed to ensure the dissolution of the calcium chloride. In the same paper Staniewicz examined the way in that the concentration of the Ca(AlCl$_4$)$_2$ affected the specific conductivity at room temperature. He recorded a maximum specific conductivity of $0.6 \times 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ at an electrolyte concentration of about 1M Ca(AlCl$_4$)$_2$. He also found that the conductivity decreased after about 1.2M. He suggested that the shape of the conductivity curve arose from several influences, namely, (i) viscosity effects, (ii) significant solute-solvent interactions, and (iii) solute-solute interactions as a result of the doubly charged Ca$^{2+}$.

Peled (3) has looked at electrolyte conductivity and the effect on it of temperature and excess aluminium chloride. He kept the concentration of aluminium chloride constant at levels of 2.2, 2.8 and 3.5M whilst he varied the concentration of calcium chloride. His results show an increase in conductivity with an increase in the concentration of calcium chloride. The highest conductivity measured at 20$^\circ$C was for an electrolyte containing 2.2M aluminium chloride. This conductivity decreased at higher concentrations of aluminium chloride. Further tests carried
out at 60°C show a maximum conductivity at an aluminium chloride concentration of 2.8M. These observations account for the fact that the solutions become more viscous with an increasing concentration of aluminium chloride. This was first noticed by Staniewicz (11).

Meitav and Peled (4) measured the conductivities of different concentrations of Ca(AlCl₄)₂ solutions (in the range of 0.38 - 1.9M ) in the temperature range of -30 to +60 °C. They found that as the temperature increased the maximum conductivity was found at higher concentrations of the electrolyte. Following the same argument they found that the conductivity for a 0.38M electrolyte increased as the temperature was reduced.

Peled (12) found that the addition of 10% v/v of sulphur dioxide to the electrolyte increased its conductivity by 40 - 50% over a temperature range of -40 to +50 °C.

This result has been confirmed by the work of Walker et al. (13). They have also measured the conductivity of a 1M solution of calcium tetrachloroaluminate in a 1:1 mixture of benzoyl chloride and thionyl chloride. They chose to mix the supporting electrolyte in the hope that the larger dielectric constant of benzoyl chloride (15) relative to thionyl chloride (9) would lead to a greater ion separation and thus increased electrolyte conductivity and capacity (14). Unfortunately, they found that this solution gave lower conductivities than a normal thionyl chloride.
supported electrolyte.

An alternative supporting electrolyte to thionyl chloride that has received attention is sulphuryl chloride. The reason for this is that when reacting with calcium metal the only products are calcium chloride and sulphur dioxide i.e.

$$\text{Ca} + \text{SO}_2\text{Cl}_2 = \text{CaCl}_2 + \text{SO}_2$$

As such there will be no elemental sulphur produced which has proved to be a problem in lithium systems, when if the cell is partly discharged two reactive substances co-exist namely lithium and sulphur.

There has been some debate in the literature as to the solubility limit of calcium tetrachloroaluminate in this solvent. Binder et.al. (15 and 16) reported that the solubility limit was of the order of 0.5M. Tulman et.al. (17) however, found that a solubility of over 1.35M was possible over a temperature range of -30 to 0°C, and even higher (up to 1.5M) at temperatures between 20 and 50°C. The differences could be due to the method of electrolyte preparation, but this would seem to be unlikely. A more probable explanation would be the water content of the solvent used. Specific conductivity measurements of calcium and lithium tetrachloroaluminates were carried out by Binder et. al. (15) The measured conductivities for the most concentrated lithium salt was found to be about an order of magnitude higher than that for a calcium salt of the same concentration. In general, the conductivity of calcium
tetrachloroaluminate, sulphuryl chloride solutions was found to be about one third of that of an analogous thionyl chloride solution. Corrosion studies also indicated that the calcium anode was attacked more aggressively in a sulphuryl chloride supported electrolyte. It is due to the above two reasons that sulphuryl chloride has lost favour in recent times and was not used for any of the work in this thesis.

**CELL PERFORMANCE**

**Open circuit voltages**

In his paper [11] Staniewicz made a study of the cell discharge products. After which he suggested that the overall cell reaction for a calcium thionyl chloride system is

\[
2\text{Ca} + 2\text{SOCl}_2 = \text{SO}_2 + 2\text{CaCl}_2 + \text{S}
\]

This follows the reaction for a lithium system closely. This reaction for the cell is as shown below.

\[
4\text{Li} + 2\text{SOCl}_2 = 4\text{LiCl} + \text{SO}_2 + \text{S}
\]

The free energy of the lithium reaction is 351 \text{kJ mole}^{-1} which is equivalent to an EMF of 3.65V. This is identical to the practical value obtained for a lithium system. By contrast the free energy of the calcium reaction is 711 \text{kJ mole}^{-1}, which is equivalent to a theoretical EMF of 3.7V. This is not seen in practice where the cell has an OCV which
has been found to increase on storage. Staniewicz (11) reported that the OCV for a newly prepared cell was 2.9 - 3V. He found that this slowly increased to a value of 3.22V after 12 hours at open circuit. Peled (18) reported similar results stating that an initial OCV of 3V was recorded and that this value increased to 3.25V after storage for between 50 and 200 hours. In the same paper Peled postulated a theory for these observations. This is outlined below but is open to debate. He suggested that the discrepancy between the theoretical (thermodynamic EMF) and observed OCV was due to an electronic leakage through the calcium chloride SEI. The components of electronic conductivity act as a load on the cell. The current resulting from the corrosion of the calcium anode will cause a voltage drop across the SEI film. This will cause a lowering of the observed OCV. Peled expressed this concept mathematically as

\[ V = E - i_{corr} R_i \]

where:

- \( V \) = measured OCV
- \( E \) = theoretical EMF
- \( R_i \) = ionic resistance of the SEI film
- \( i_{corr} \) = corrosion current density

The corrosion current density can be calculated from Ohm's Law if the electronic resistance (Re) is known,

\[ i_{corr} = \frac{V}{Re} \]
The ionic transport number \( (t_i) \) is related to both the ionic \( (R_i) \) and the electronic resistance of the calcium chloride SEI. Peled states this relationship to be,

\[
\frac{1}{R_i}t_i = \frac{1}{R_i + \frac{1}{Re}}
\]

from which the observed OCV and theoretical EMF can be linked i.e. \( V = t_iE \)

Using the above reasoning Peled estimated the ionic transference number for a calcium tetrachloroaluminate thionyl chloride system as 0.88. The increase in OCV on standing has also been explained (18) in that when a calcium anode is first immersed in the electrolyte the corrosion will be fast as the calcium oxide layer (built up during storage in air) is dissolved and replaced with calcium chloride. This rapid corrosion will result in a very disordered SEI and one in which the electronic conduction will be increased. If the electronic conduction is large then \( t_i \) will be small. Consequently the observed voltage is reduced. As time passes the calcium chloride SEI becomes more ordered and the corrosion rate decreases (19). This will result in a decrease in the electronic resistance and hence an increase in the observed OCV. Were it possible to reduce the electronic resistance to 0, then \( t_i \) would reach unity and the observed voltage of the cell would be the same as the theoretical EMF (i.e. 3.7V) as is seen with Lithium cells.
Until recently the carbon black most used as a cathode material in calcium thionyl chloride cells was Shawinigan Acetylene Black (SAB). It has a low surface area of $60 \text{m}^2\text{g}^{-1}$. More recent work has shown that higher surface area carbon blacks lead to better discharge characteristics (13 and 20). The carbons are best used as a mixture of both low and high surface area, since this gives both an increased performance and the greater mechanical strength and integrity of SAB. High surface area carbon blacks that have received attention are Ketjenblack EC DJ600 and Black Pearls 2000.

In order to give the cathode enough mechanical strength for easy handling it is customary to use a polymeric binder (usually PTFE). The polymer is filamentous and binds together the carbon particles, thus allowing the carbon to expand during discharge without mechanical breakdown. The filamentary nature of the binder also minimises the mechanical blockage of the active carbon surface (21). The amount of PTFE added has not been consistent between workers. Dey (22) suggested that at least 10% by weight should be used in the carbon. As PTFE cannot hold the calcium chloride produced at the cathode any extra PTFE used will result in a decrease in the cell capacity. Gilman and Wade (23) have reported that the optimum concentration of PTFE is 10.7% by weight. At Loughborough we have found that only 5% by weight will suffice (24).
carbon in the cathode is advantageous since it will result in greater cell capacity for the reason stated above.

Staniewicz (11) showed that the capacity of cathodes in calcium cells was less than that for lithium. He states that the capacity is directly related to the molar volume of the discharge products per equivalent of charge passed. The equivalent volume of lithium chloride is given as 20.5 cm$^3$ whereas that for calcium chloride is 25.8 cm$^3$. The reduced carbon capacity will also be related to the mobility of the cations in the electrolyte. The Ca$^{2+}$ ions will have a lower relative mobility than the Li$^+$. Binder et. al. (15) compared discharges at current densities of 5 mA cm$^{-2}$ of cathode area, with both calcium tetrachloroaluminate and lithium tetrachloroaluminate. The cells were fabricated using SAB cathodes and either calcium or lithium anodes. They found that the calcium cells had only half the discharge life of the lithium cells. Walker et. al. (13) has shown that mixing high and low surface area carbon blacks (Black Pearls 2000 and SAB) gives increased performance. Addition of sulphur dioxide to the electrolyte further enhanced the cathode performance. He found that the cathode load potentials and the life were nearly equal to the analogous lithium system.

Walker et. al. (25) has tried to add substances to ease the reduction of thionyl chloride at the cathode. He used SAB cathodes to which he added either TiO$_4$ which has a high electrical conductivity or LaNiO$_3$ which is an oxygen
reduction catalyst. He discharged the cells at 20 mAcm\(^{-2}\) but found that the additives only slightly improve the on load voltages. Additions of titanium oxide marginally extended the cathode life.

**DISCHARGE CHARACTERISTICS**

Initial discharges were conducted by Staniewicz (11) who discharged flooded cells at a rate of 0.7 mAcm\(^{-2}\) of calcium area. He noted that the cathode discharge was fairly constant but that the anode became increasingly polarised as the SEI film became thicker. He found that the discharge of the anode was not uniform but proceeded by pitting over the anode surface. This was observed to be particularly acute at the edges. Failure of the cells was due to corrosion which either lead to detachment of the calcium anode from the nickel lead or due to the disintegration of the anode itself. He concluded that, based on the number of coulombs passed, only 50% of anode utilisation was achieved. This capacity was maintained after 1 month of storage. Discharge times of cells stored either at an elevated temperature or for longer times at room temperature showed a marked decrease in their performance. In these cases the capacity was only 40% of the calculated value. He attributed this to a continued attack by the electrolyte on the calcium anode. Other electrolytes were evaluated namely Ca(FeCl\(_4\))\(_2\), Ca(SbCl\(_6\))\(_2\) and LiAlCl\(_4\). The Fe and Sb based electrolytes resulted in a poor performance, lower both in terms of on
load voltage and calcium utilisation. The Li based electrolyte however resulted in a better performance than the analogous calcium one.

Higgins and Cloyd (26) performed discharge tests on 1/2 "D" sized cells which they rated at 3.5Ahr and large 600Ahr cells which contained a 1.4M lithium tetrachloroaluminate electrolyte. They varied the rate of discharge for the 1/2 "D" sized cell between 0.05 and 1.00A. The effect of temperature on the discharge was also investigated in the range of -29 to +40°C. They found that at a constant temperature increasing the discharge rate resulted in a decrease in the cell capacity. The highest capacities were obtained at a temperature of 20°C. For the 600Ahr lithium electrolyte cells they evaluated both low and high surface area cells. These were both discharged at a current of 5A, the high surface area cell discharge was carried out at a temperature of 20°C. Under these conditions the cell realised 400 Ahr. By contrast a low surface area cell under the same load and discharged at a temperature of 30°C gave a capacity of 630 Ahr above the 2V cut off voltage. In addition it was noted that 80% of this discharge was at a potential greater than 2.5V. Higgins (27) produced a larger cell with a theoretical capacity of 7500Ahr. When discharged it was found to only give 5600Ahr. He explained the discrepancy as being due to an elevated temperature within the cell which during the discharge was an average of 43°C. The effect of temperature and electrolyte composition on discharge performance was investigated by Peled et. al. (3).
They discharged cells at 23°C and 60°C and found that a higher capacity was achieved at the higher temperature. A cell which has a higher electrolyte conductivity was also found to give a greater capacity (this has been commented on earlier).

Further cell discharges were carried out by Meitav and Peled (4) on cells which either contained a 1.3M or 0.7M calcium tetrachloroaluminate electrolyte. The cells were discharged at temperatures of 60, 25 or -20°C. Their observations indicated that the preferred electrolyte concentration for the two higher temperatures was 1.3M. By contrast discharges at -20°C showed that the 0.7M electrolyte gave an enhanced performance. At 25°C and with a 1.3 M electrolyte a discharge rate of 1mA cm⁻² gave a capacity of 35mA Hr. The cell was found to deliver around 60% of its capacity at the higher rate of 11mA cm⁻².

Peled et al. (12) has in addition prepared prototype "C" sized cells containing a 0.95M calcium electrolyte. They found at room temperature that the cell showed energy and power densities similar to that of a lithium sulphur dioxide battery. The cell was also found at a number of different discharge rates to exhibit an increase in capacity with an increased cathode porosity from 82% to 88% and also with a decrease in the amount of teflon binder used from 12% to 6%. In addition the "C" sized cell was found to be able to maintain a current above 1A continuously over a temperature
range between -40 and +80°C.

**Anode Corrosion**

Corrosion of the calcium anode has always been identified as a major problem with the calcium thionyl chloride system. In that at open circuit this corrosion is of such an extent that it drastically reduces the shelf life of the cell. The shelf life has been predicted as being only two years. This compares most unfavourably with a lithium thionyl chloride cell which has a shelf life of at least ten years. Staniewicz (11) stated that the presence of any excess aluminium chloride present in the electrolyte would exacerbate the corrosion problem since it would attack the calcium anode and in doing so form calcium chloride. The solution to this problem he felt was to make up the electrolyte with an excess of calcium chloride to ensure that no free aluminium chloride remains. In general there are two ways of dealing with the corrosion of the anode and these can be grouped into physical and chemical methods.

(i) the physical approach.

This would normally involve the coating of the anode with a protective layer, for example a polymer. The polymer that received most attention is cyanoacrylate which has also been employed in lithium systems. This approach is based on the idea that if the calcium anode can be isolated from the electrolyte the corrosion cannot start. However there is a significant problem in that the layer can only provide this protection once. As soon as it is removed i.e. once current...
is drawn then it is not able to reform and thus corrosion will continue apace. Hence the polymer protection is of no use if the cell is required for intermittent discharge duty. In addition the cell will exhibit a considerable voltage delay when first placed on load as the polymer film is cracked off and removed. This voltage delay will be far more pronounced at higher current densities. These problems have led to a much reduced interest in this method of anode corrosion suppression in recent years.

(ii) The chemical approach.

This method can involve changes to the cation, anion or additions to the electrolyte as a whole. Staniewicz (11) concentrated on replacing the aluminium chloride in his efforts to reduce the rate of open circuit corrosion. He prepared the following calcium electrolytes, Ca(SbCl₆)₂ and Ca(FeCl₄)₂, and assessed their corrosion rates relative to pure thionyl chloride and a calcium tetrachloroaluminate electrolyte. In both cases he found that the rate of corrosion was greater than the tetrachloroaluminate electrolyte, and much greater than the pure solvent. In addition he prepared a tetra ethylammonium tetrachloroaluminate electrolyte, in the hope that should Ca²⁺ ions in the bulk solution contribute to a catalytic corrosion, then replacing them with a non metallic cation would reduce the corrosion rate. In practice he found that the corrosion observed in this electrolyte was more advanced
than that for a normal electrolyte. Staniewicz concluded that open circuit corrosion occurred during storage of the electrolyte and that this corrosion occurred at a faster rate when the cell was placed on load. Higgins and Cloyd (26) prepared cells and stored them for a six month period. They noticed that there was a significant performance variation occurring amongst these stored cells. In addition they doped calcium anodes with compounds thought to be contaminants, such as iron. The electrolyte attack on the calcium was then estimated and they concluded that the corrosion of the system might not be inherent but due to other impurities in the anode. Tulman et. al. (28) conducted tests on calcium tetrachloroaluminate electrolytes at room temperature and at 70°C. They suggested a useful shelf life of 1.5 to 2 years. Staniewicz (11) tried to reduce the corrosion by using annealed samples of calcium in which he had removed the surface coating by chemical means, he thought that work hardening and surface roughness of the calcium would result in a lowered contact area between the current collector and the calcium anode. By annealing the calcium he hoped to gain a better contact and as a consequence, a higher utilisation of the anode. Peled (29) has tried to reduce the calcium corrosion by using strontium and barium tetrachloroaluminate electrolytes. He reports a changed SEI structure in which there is interchange between the metal in the electrolyte (i.e. strontium or barium) and the anode. As a consequence the SEI is doped with either strontium chloride or barium chloride and he claims that
this leads to a reduced corrosion of the calcium anode. These conclusions have recently been called into question by Walker et al. (30) who prepared cells with a strontium tetrachloroaluminate electrolyte. They have estimated that the useful shelf life of these cells is only of the order of 10 months. This is considerably lower than that for a normal calcium tetrachloroaluminate electrolyte and so does not appear to be a viable alternative.

Safety of Cells

The principal advantage of a calcium anoded cell over an analogous lithium cell can be expressed in terms of its safety. Problems due to the lithium anode have been detailed above, they are principally because "mossy" lithium metal can be plated out if a cell is reversed and the lithium anode has the relatively low melting point of 180°C. Higgins and Cloyd (26) have examined calcium anoded cells and assessed their safety relative to lithium technology. In their tests they retained the lithium tetrachloroaluminate electrolyte and changed the anode material to calcium. They constructed cells ranging from between 3.5 AHR up to 600AHR. Cells were prepared having both a low or high surface area of calcium. The abuse tests consisted of a short circuit through a 2 milliohm resistor, reversal of the cell, charging of cells, incineration of a cell, and damaging the cell casing either by crushing it with a hydraulic ram or puncturing it using a steel spike. They even subjected cells to penetration by firing bullets at the casings. They
concluded that for a low surface area design of cell no response was observed for any of the tests. Penetration of the casing led only to an exposure to electrolyte fumes with no problems traceable to the calcium anode. In addition they stated that storage capability could be good for up to the six months of the test. In a later paper Higgins (31) prepared cells up to 22kW Hr and subjected these to abuse. He concluded that the cells were not sensitive to internal or external short circuit and were practically incapable of being reversed. These results eliminate any fear that problems might arise due to a scale effect. There was no evidence of thermal runaway in any of the cells that he tested. Peled (32) has tried to reverse and charge fully discharged cells with very little effect. He used a 0.9 M calcium tetrachloroaluminate electrolyte and found that no electrolyte bubbling or cell venting was observed. He used charging potentials up to 25V and reversed cells up to 28 V. They emphasised that any other lithium cell or even a regular non- lithium cell under similar conditions would explode, or at the very least would be subject to venting.
Chapter 3

Materials and Specifications

The following is a list of compositions and specifications of chemicals and apparatus used in the work that is presented in the following chapters.

Chemicals

Calcium: New Met, analysis performed at Alcan's labs (33) showed the following composition of impurities.

<table>
<thead>
<tr>
<th>Element</th>
<th>Si &amp; Fe &amp; Cu &amp; Mn</th>
<th>Mg</th>
<th>Al</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (wt%)</td>
<td>-----</td>
<td>0.10</td>
<td>0.18</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

Thionyl Chloride: Fluka Chemika puriss grade (vacuum distilled)

Calcium Chloride: Fluka Chemie purum grade

Aluminium Chloride: Fluka Chemie puriss grade

Strontium Chloride: Ventrum GMBH

Polishing Oil: Bueker polishing oil, Illinois, USA

Abrasive Discs: 3M Wet and Dry

Separator paper: Saffil "Al2" Non Woven ceramic separator paper.

Cathode carbons: Blended with 5% by weight Fluon, ICI (a 60% PTFE in aqueous suspension), in propan-1-ol. The solvent is then removed and the carbon dried in an oven. Shawinigan Acetylene Black (SAB): Shawinigan Carbide inc. Canada.

Ketjenblack EC DJ600: Akzo Chemie, Walton on Thames, Surrey.
Nickel (Test cell tags and current collectors): Expanded Metal Co., Hartlepool.

Silver/silver chloride reference electrode: Silver wire from Aldrich polarised in a solution of iron(III) chloride and hydrochloric acid.

Sulphur Dioxide: BDH lecture sized cylinders.

**Apparatus**

Potentiostat: Thompson precision ministat.

Digital Multimeters: Beckman models tech 310 and 3050

For Cyclic Voltammetry,

Thompson DRG16 Ramp Generator.

Thompson Rotating Disc Electrode system.


For Discharge Experiments

Philips PM 8252 Dual Pen Chart Recorder.

For Impedance Measurements

Solartron 1186 Electrochemical Interface.

Solartron 1250 Frequency Response Analyser.

Kemitron microcomputer.

Dacoll 2000 series Visual Display Unit.

Thompson DRG16 Ramp Generator.

Thompson Rotating Disc Electrode System.

For Electrolyte Solubility Measurements

Pye Unicam model PU8600 UV/Visible spectrophotometer.

Philips PU9100 Atomic Absorption spectrophotometer.

Other chemicals used were all analar (or higher) grade.
Chapter 4
Corrosion Suppression of Calcium Anodes at Open circuit

Introduction

Concern for the safety of lithium oxyhalide cells has led to a search for alternative anode materials. A well documented alternative is calcium but this exhibits a faster corrosion rate than lithium. This corrosion is a fundamental short-coming of the calcium thionyl chloride system and must be improved before exploitation is feasible (see chapter 2).

Corrosion normally conjures up a picture of the oxidation of a metal by oxygen in water. In fact it is much more general and takes the form of a redox reaction taking place on an electronically connected surface. In the case of calcium cells these redox processes are the reduction of thionyl chloride and the oxidation of calcium to calcium chloride. As the corrosion process continues the SEI (corrosion product layer) will build up, causing a degree of passivation and a slowing of the rate of corrosion. For a calcium system this model is complicated by any solubility of the SEI or mechanical break down of the film. The amount of surface coverage of the anode by the SEI and the composition of the protecting film will also affect the rate of corrosion. These factors make the prediction of corrosion
rates from thermodynamic and kinetic data unreliable so that the only accurate method of determining the corrosion rate is by experiment.

**Initial Investigation**

A calcium disc cut from foil supplied by New Met was divided in two, and each half was placed in a sample tube. To one tube a sulphur dioxide saturated 1.0M electrolyte was added whilst the other was placed in pure 1.0M electrolyte. After only 75 minutes the effects of the two electrolytes were noticeable, in that dark corrosion patches had formed on the sample exposed to the normal electrolyte. The corroded areas were in the form of straight lines that seemed to follow the striations which would be caused by the mechanical rolling of the calcium into a film. The disc in the sulphur dioxide saturated electrolyte showed only very slight corrosion along the line of cut of the disc. The rest of the sample remained visually bright and uncorroded.

The results looked very promising and an obvious way to carry these investigations forward was to record samples at varying time intervals to see if the visual difference seen in this test was maintained at longer time intervals. The results can be seen in fig 4.1. The ten numbered samples are shown as matched pairs, the samples numbered 1 to 5 were corroded in a normal 1.0M electrolyte whereas those numbered 6 to 10 were exposed to a saturated sulphur dioxide electrolyte. These samples confirmed the initial results in that the sulphur dioxide saturated samples appeared to have
Fig 4.1

<table>
<thead>
<tr>
<th>No.</th>
<th>Time/hours</th>
<th>No.</th>
<th>Time/hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>48</td>
<td>7</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
<td>8</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>168</td>
<td>9</td>
<td>168</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>10</td>
<td>240</td>
</tr>
</tbody>
</table>
corroded to a far lesser degree than those placed in a normal 1.0M electrolyte. These visual results were very encouraging and it was decided to set up longer term corrosion tests and to monitor the corrosion in a more quantitative manner. At first it was thought that the corrosion could be followed by a weight gain of calcium discs, since the corrosion product is calcium chloride. It was argued that the reaction of:

\[ \text{Ca} \quad \rightarrow \quad \text{CaCl}_2 \]

could be monitored since the increase in weight would be virtually 2 to 1 (in terms of molecular weight 40 \( \rightarrow \) 110). This would not however compare too favourably with the corresponding lithium reaction where the lithium chloride reaction product exhibits a weight gain of 5 to 1. Reproducibility was very hard to obtain in terms of the weight gain of samples. On further deliberation it was reasoned that the corrosion would cause some of the calcium chloride reaction product to become physically detached from the sample. Either by the method of the corrosion or alternatively in the way that the samples were treated in order to remove traces of the electrolyte that might remain prior to the weight being recorded. This would result in a false lower rate of corrosion since the recorded weight gain would be considerably less than the true gain. An alternative method of monitoring the degree of corrosion of these samples was sought. The most obvious substitute was to remove the corrosion products on the calcium sample and then
to measure a weight loss of the sample. Thus the degree of corrosion could be measured from the amount of calcium lost during the experiment.

**Longer term open circuit corrosion experiments**

The optical data (fig 4.1), provided encouraging results for the reduction of the open circuit corrosion by means of the saturation of the electrolyte at atmospheric pressure with sulphur dioxide. Samples were stored in an excess of electrolyte to provide a more aggressive environment than that found in the more normal electrolyte starved configuration of a commercial cell.

Calcium metal foil (New Met) was punched into discs which were then polished mechanically in a dry air (10-20ppm water) glove box. The discs were then degreased by stirring in acetone (for 3-4 minutes) before being individually weighed and then placed either in the sulphur dioxide-containing electrolyte or a normal 1.0M electrolyte which was used as a control.

We chose a Ca (AlCl₄)₂ concentration of 1.0M as a compromise for our calcium corrosion studies at room temperature since Meitav and Peled (4) had shown that a 0.7M electrolyte gave a better performance at lower temperatures whereas for higher temperatures they recommended a 1.3M electrolyte. At higher electrolyte concentrations the conductivity has been shown to decrease (25) due to ion pairing and the increased viscosity of the solution.
The electrolyte was prepared by first dissolving aluminium chloride into thionyl chloride and then adding calcium chloride. A 10% excess calcium chloride was added to ensure electrolyte neutrality. Without the calcium chloride there was a danger of forming free Lewis acid. The mixture was then refluxed for 6 hours before being returned to the dry box for filtering to remove the excess calcium chloride. Staniewicz (11) suggested that any excess aluminium chloride might react directly with the calcium metal anode.

\[ 3\text{Ca} + 2\text{AlCl}_3 \longrightarrow 2\text{Al} + 3\text{CaCl}_2 \]

This would be in addition to the aluminium chloride attacking the calcium chloride of the protective S.E.I. (Solid Electrolyte Interface i.e. the film on the calcium surface) to form the tetrachloroaluminate, thus removing it and leaving the bare metal open to attack by the solvent. When anode samples were removed from the electrolyte they were first washed three times in pure thionyl chloride, then dried and stored in a separate electrolyte-free dry box in sealed containers in order that the corrosion did not continue after the time of measurement.

It had been decided to follow the degree of the corrosion by means of preferentially dissolving the calcium chloride SEI away from the calcium metal using acetone. The acetone was purified and dried using a
procedure outlined by Vogel (34) which involved refluxing with potassium permanganate then drying over potassium carbonate before being fractionated using a Vega column. The acetone was then stored over 0.4 nm molecular sieve in the glove box. Acetone was chosen as the solvent since earlier tests had shown that calcium metal had no measurable solubility in it. The discs were periodically removed from the solvent, dried, and weighed. This process was repeated until no weight change could be detected.

Discs of calcium prepared as outlined above were placed in either the sulphur dioxide saturated or the unmodified electrolyte and their weight losses were recorded. The results are shown graphically in figure 4.2.

Results and Discussion

As can be seen the difference in corrosion between the two electrolytes is striking. Firstly the difference in the gradient of each line (fig 4.2) suggests that the reduction in corrosion by the sulphur dioxide-containing sample will be even more marked at longer times, and secondly that the sample had corroded more after 96 hours in the unmodified electrolyte than the sulphur dioxide saturated electrolyte sample had done after 1944 hours.

We also studied the corrosion with and without sulphur dioxide by means of electron microscopy. Results from this investigation support those obtained
Open Circuit Corrosion Data

Figure 4.2

Weight Loss / mg cm\(^{-2}\)

1.0M Electrolyte

1.0M Sulphur Dioxide saturated Electrolyte

Time / Hours
from the weight loss experiments and indicate that in the ordinary electrolyte the SEI appears to have an open porous corrosion layer. This allows continuous attack of the underlying metal by the electrolyte.

By contrast the sulphur dioxide saturated electrolyte appears to engender a more compact tenacious film which seems to protect the bare metal from the worst corrosive effects of the electrolyte.

A selection of the micrographs obtained are presented in chapter 9. Micrographs are shown at various times up to 100 days of samples corroded both in the normal electrolyte and one that had been saturated with sulphur dioxide.

The pictures show that the porous layer of the SEI can be seen to be developing in a different way from the earliest times rather than the SEI establishing itself, and then being attacked by the sulphur dioxide in the electrolyte. This observation is in agreement with the weight loss data since the difference in weight loss is apparent from the start of the experiment.

Conclusions

As can be seen from the results after a period of 3 months the corrosion of the calcium anode has been reduced from 1.02 mg cm\(^{-2}\) in an unmodified electrolyte to 0.55 mg cm\(^{-2}\) in a sulphur dioxide saturated one. This indicates a substantial reduction in corrosion approaching a factor of 2. The weight loss experiments, supported by scanning electron micrographs, confirm the view that the addition of sulphur dioxide changes the corrosion of
the calcium. This can be seen in the changed physical appearance of the surface film.
Chapter 5

Electrolytes for calcium anoded cells

Introduction

The two main catholyte solvents used to date for these cells are thionyl chloride and sulphuryl chloride. The classical method of preparation of supported, thionyl chloride electrolytes has been discussed in detail in the literature review. The relative advantages and disadvantages of sulphuryl chloride has also been outlined. The work of this thesis has been solely concerned with the application of thionyl chloride, sulphuryl chloride has not been used for any of the cells prepared. This was primarily because of the problems associated with sulphuryl chloride that have again been considered in the literature review (chapter 2).

Thionyl chloride although providing a reasonable ionising medium for chemical reactions suffers from an inability to dissolve many salts which effectively limits its usefulness as a non aqueous solvent. In appearance, thionyl chloride is a colourless liquid having a melting point of $-104^\circ$C, and a boiling point of $75.6^\circ$C. It has a density of $1.629 \text{ g cm}^{-3}$ at $25^\circ$C and a dipole moment of $1.58\text{D}$ (35).

Thionyl chloride is a highly reactive substance. In the presence of metal or metal oxides it forms the appropriate metal chloride. Thionyl chloride as an electrolyte is
restricted in its application by having a low specific conductance ($3.5 \times 10^{-9}$ ohm$^{-1}$ cm$^{-1}$). Its performance is enhanced by the addition of current supporting Lewis acids. Calcium systems have previously concentrated on the use of aluminium chloride, lithium systems have used a variety of Lewis acids such as antimony penta- and tri-chlorides, iron tri-chloride and tin (IV) chloride. These have the effect of increasing the relative concentration of $\text{SOCl}_2^+$ ions. Their mode of action is explained as follows.

The accepted definition of acids and bases was proposed by J.N. Bronsted and T.M. Lowery in 1923. According to this an acid maybe defined as a substance which has a tendency to lose a proton, whereas conversely a base maybe described as a substance which has a tendency to gain a proton.

This definition has been extended so that any substance which increases the number of solvent cations is considered to be an acid while a substance giving rise to an increase in the number of solvent anions is a base.

In 1938 Lewis (36) published a different theory of acids and bases which is sometimes referred to as the electronic theory. This considers that an unshared electron pair in a base molecule is accepted by an acid molecule, in doing so it forms a covalent link. As such an acid maybe defined as a substance which can accept a lone pair of electrons and a base is a substance which can donate a lone pair.

Lewis acids cannot be as easily classified as simple
proton acids because the relative acid strength will vary from one solvent to another. One method of classification was put forward by Pearson (37) who considered the polarisability of the base. He defined "soft" bases as those in which the donor atom has a high polarisability, low electro-negativity and is easily oxidised. Examples include I\(^-\), SCN\(^-\), S\(^2-\). Hard bases not surprisingly are defined as those with opposite properties and include OH\(^-\) and F\(^-\). Hard and soft acids can be defined as compounds which will form stable complexes with hard and soft bases respectively. Hard acids include small non-polarisable metal cations with high oxidation numbers and inert gas structures, soft acids include the larger metal ions for example Cu\(^+\), Ag\(^+\) and Hg\(^{2+}\).

The supporting electrolyte thionyl chloride has a very low conductivity due to a slight self ionisation.

\[
\text{SOCl}_2 \rightleftharpoons \text{SOCl}^+ + \text{Cl}^-
\]

The self ionisation is too small to allow for the formation and reactions of acids and bases. In such solvents these reactions are initiated by the solvation of dissolved compounds. For a calcium system the usual Lewis acid used is aluminium chloride. Adding this to thionyl chloride results in the transfer of chloride ions from the solvent to the solute. This reaction accounts for the relative increase in the concentration of SOCl\(^+\), as is shown below:

\[
\text{AlCl}_3 + \text{SOCl}_2 \rightleftharpoons [\text{SOCl}]^+ [\text{AlCl}_4^-] \rightleftharpoons \text{SOCl}^+ + \text{AlCl}_4^-\]
Experimental

The preparation of a calcium electrolyte has been discussed in the review section, (chapter 2). The addition of sulphur dioxide has been shown to increase the discharge performance (capacity) of the cell (see chapter 6). One of the effects of sulphur dioxide was thought to be an increase in the solubility of calcium chloride in the electrolyte. It was decided to test whether the solubility of calcium chloride was the key to enhancing the performance of the system. To this end balanced electrolytes were prepared containing calcium, sodium and strontium tetrachloroaluminates. The term balanced refers to the amount of metal chloride used in the preparation of the electrolyte. Thus for a calcium electrolyte, only enough calcium chloride was added to balance the aluminium chloride.

Samples of the electrolytes were then taken and saturated with calcium chloride. The excess solubility of calcium chloride in the electrolyte was then measured by measuring the total calcium content. In the case of a calcium electrolyte, the calcium required to form the electrolyte was subtracted, leaving the remainder as the excess solubility of calcium chloride.

To ensure that the prepared electrolytes were balanced, the amount of aluminium chloride was measured using a colourimetric determination (38). This used Eriochrome
Cyanine R as the complexing agent. The system consists of two tablets. The first, a buffer which is added to 10ml of solution and mixed to dissolve. The second tablet is then added and the sample is placed in the dark to allow the colour to develop. The colour of an aliquot of this solution is then measured against an air blank in a U.V. / visible spectrophotometer. The absorbance maximum was measured at 535 nm. Standard solutions of aluminium with a concentration below 10ppm were only thought to be reliable for the day on which they were prepared. A calibration graph was prepared for various aluminium concentrations and the results were plotted against the absorbance measured at a wavelength of 535 nm. The graph was reproducible to within 2-3% up to concentrations of 0.1ppm. After this the linearity of the graph is disturbed. Hence when the level of aluminium was determined in the various electrolytes the samples were diluted sufficiently to be measured in the region below 0.1ppm.

A balanced electrolyte of sodium tetrachloroaluminate was prepared by first stirring sodium chloride into the thionyl chloride already containing aluminium chloride for a prolonged period (over 50 hours) and then placing the solution in an ultrasonic bath to ensure complete solubility of the sodium chloride in the electrolyte. A sample of this was then saturated with sodium chloride. This was achieved by adding more sodium chloride and then returning the sample to the ultrasonic bath. The original electrolyte was then taken and hydrolysed to allow determination of the sodium
(by atomic absorption) and aluminium contents. These showed that the electrolyte was balanced in that there was no excess of either aluminium chloride or sodium chloride.

The sample of the electrolyte that had been saturated with sodium chloride was then analysed for sodium (again using atomic absorption spectroscopy). The results showed that there was no noticeable difference in the concentration of sodium ions. This is a very interesting result in that there is no excess capacity for sodium chloride in a sodium tetrachloroaluminate - thionyl chloride electrolyte. Hence in a cell under discharge conditions when thionyl chloride is reduced at the carbon cathode there is no solubility for the sodium chloride. It will thus be deposited at the front face of the carbon rather than utilising the full volume of the carbon matrix, leading to the premature failure of the cell due to cathode blocking. As the discharge results (chapter 6) show the cell is carbon limited.

In the same way as the sodium chloride content was measured other electrolyte types were considered, namely strontium tetrachloroaluminate and calcium tetrachloroaluminate. Potassium tetrachloroaluminate was also considered but it proved impossible to prepare a balanced 1.0M electrolyte in thionyl chloride in that the potassium chloride could not be dissolved into the electrolyte in sufficient quantity to prepare the balanced electrolyte, so that any results obtained would be worthless. Magnesium tetrachloroaluminate was not considered
because Peled (39) had shown that the corrosion in this electrolyte was too rapid to make a viable cell using this system. The results of the calcium chloride solubility in the electrolytes are presented in table 5.1.

The solubility of calcium chloride was measured at 0.018M in a 1.0M calcium tetrachloroaluminate electrolyte. By comparison the solubility of lithium chloride in a lithium tetrachloroaluminate electrolyte has been measured by Hagan and Hampson (40) to be 0.16M.

Table 5.1

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>Solubility of Calcium Chloride / M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(AlCl₄)</td>
<td>0†</td>
</tr>
<tr>
<td>Ca(AlCl₄)₂</td>
<td>0.018*</td>
</tr>
<tr>
<td>Ca(AlCl₄)₂, SO₂ sat.</td>
<td>0.033*</td>
</tr>
<tr>
<td>Sr(AlCl₄)₂</td>
<td>0.027</td>
</tr>
</tbody>
</table>

† Above mean of 6 tests reproducible to 0.002M.

* Denotes excess solubility over and above the amount necessary to balance the electrolyte.

The above table indicates that the solubility of calcium chloride in a calcium tetrachloroaluminate electrolyte is almost doubled by the saturation at atmospheric pressure with sulphur dioxide (10 - 12 % V/V). In addition a strontium tetrachloroaluminate electrolyte exhibits 1.5 times the solubility of the baseline balanced calcium system.

The greater the capacity for calcium chloride in the electrolyte the greater the performance, as long as the cell
is cathode limited (chapter 6). This will be because the local solubility of the electrolyte in the immediate vicinity of the anode will not be so easily exceeded. Also the packing of the carbon cathode will be more efficient and thus the performance will increase. This is discussed in greater detail in the discussion of the results in chapter 10.
Chapter 6

Discharges of cells

Cell discharges were performed on a number of different electrolyte systems in order to evaluate the factors contributing to improved on load performance for a calcium anoded cell. A cell was designed in order to perform these tests, so that all other critical cell components could be kept constant (fig 6.1). This was done to ensure that any improvement in the discharge time would be solely attributable to the electrolyte. The cell was constructed out of P.T.F.E. and was held together with three steel bolts, tightened to a constant torque. The electrodes consisted of a calcium foil anode, carbon cathode and a silver/silver chloride reference. The calcium anodes were made from a calcium foil (New Met) which was punched into discs. These discs were mechanically abraded using a fine grade emery paper and then degreased in acetone. This was done to ensure a reproducible sample of calcium. Electrical contact to the anode and cathode was achieved by means of a nickel plug for the cathode and a gauze of the same metal for the anode. Two pieces of a ceramic separator (Saffil grade A12) were sandwiched between the electrodes to prevent a short circuit. A small hole in the top of the cell allowed the electrolyte to be added after assembly. The cell was discharged in a dry air glove box connection to the outside.
Cell Design used for discharge experiments

Figure 6.1
load being applied via a feed-through to a Thompson Ministat Potentiostat. The potentiostat was connected to act as a galvanostat so that the load on the cell could be held constant. The benchmark load chosen was equivalent to 10mA cm\(^{-2}\). The traces were recorded on a Philips PM 8252 dual-pen recorder so that referenced measurement of both the calcium and carbon electrodes could be made.

The referenced cells showed that for a normal 1.0M Calcium tetrachloroaluminate electrolyte the cell was anode limited in that the anode reference voltage was seen to fail first and cause the failure of the carbon.

Discharges using a balanced 1.0M calcium tetrachloroaluminate electrolyte showed an increased performance with respect to both on load voltage and particularly in the time to cell failure. Interestingly the failure mode of the cell changed from an expected anode failure to a cathode failure.

Adding sulphur dioxide to a stock (i.e. one saturated with calcium chloride) calcium tetrachloroaluminate electrolyte also changes the failure from anode to cathode, whilst at the same time increasing the cell performance. This would suggest that increasing the solubility of calcium chloride, the discharge product, leads to enhanced performance and greater calcium utilisation. To test this theory a balanced electrolyte containing no sulphur dioxide was taken and 0.04M of excess aluminium chloride was added. The capacity of the electrolyte for calcium chloride would
therefore be increased, and if solubility is the key then an enhanced discharge performance should result. The trace shows that an increase in discharge time occurs. The significance of this result is discussed later in chapter 10.

Saturating a balanced electrolyte with sulphur dioxide leads to the expected carbon failure and a further improved discharge performance both in terms of on load voltage and time to failure.

Saturating an electrolyte first with sulphur dioxide and then with calcium chloride resulted in a performance that was poorer than an electrolyte saturated first with calcium chloride and then with sulphur dioxide.

In addition to the calcium tetrachloroaluminate containing electrolytes, balanced electrolyte systems were prepared containing strontium tetrachloroaluminate. This electrolyte was tested both with and without the addition of sulphur dioxide, as well as the analogous potassium and sodium electrolytes.

The potassium tetrachloroaluminate electrolyte was disappointing in that an on load plateau voltage could not be maintained. On closer inspection of the electrolyte it was found that the potassium chloride was not soluble to 1.0M in thionyl chloride/aluminium chloride, indicating that the electrolyte was less than 1.0M. The results of the discharge performance are summarised in table 6.1.

Figs. 6.2 --> 6.10 depict typical discharge traces showing the overall cell performance and referenced anode
and cathode measurements using the cell described in fig 6.1, for the electrolytes listed in table 6.1

**TABLE 6.1**

<table>
<thead>
<tr>
<th>Electrolyte Composition</th>
<th>Solubility of CaCl₂/g dm⁻³</th>
<th>Time to 2V Failure /mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>For 1.0M Ca(AlCl₄)₂:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sat CaCl₂</td>
<td>-----</td>
<td>46 (Fig 6.2)</td>
</tr>
<tr>
<td>Balanced</td>
<td>1.98</td>
<td>105 (Fig 6.3)</td>
</tr>
<tr>
<td>sat CaCl₂ then sat SO₂</td>
<td>-----</td>
<td>74 (Fig 6.4)</td>
</tr>
<tr>
<td>sat SO₂ then sat CaCl₂</td>
<td>-----</td>
<td>61 (Fig 6.5)</td>
</tr>
<tr>
<td>Balanced sat SO₂</td>
<td>3.63</td>
<td>119 (Fig 6.6)</td>
</tr>
<tr>
<td>0.04M xs AlCl₃</td>
<td>(2.2O)</td>
<td>120 (Fig 6.7)</td>
</tr>
</tbody>
</table>

For 1.0M Sr(AlCl₄)₂:

| Balanced                | -----                       | 90 (Fig 6.8)             |
| Balanced SO₂            | -----                       | 127 (Fig 6.9)            |

For 1.0M Na(AlCl₄):

| Balanced                | -----                       | 26 (Fig 6.10)            |
1.0M Calcium electrolyte calcium chloride saturated

Figure 6.2
1.0M Balanced calcium electrolyte

**Figure 6.3**

![Graph showing cell voltage, calcium/ref, and carbon/ref over time.](image_url)
1.0M calcium electrolyte calcium chloride and sulphur dioxide saturated

Figure 6.4
1.0M Saturated first with Sulphur dioxide and then with Calcium Chloride

Figure 6.5
1.0M Balanced calcium electrolyte sulphur
dioxide saturated.

Figure 6.6
1.0M Calcium Electrolyte containing 0.04M excess of Aluminium Chloride.

Figure 6.7

![Diagram showing cell voltage over time for calcium and carbon ref, with a load of 10 mA cm⁻².](image)
1.0M Strontium Electrolyte discharge

Figure 6.8

![Graph showing cell voltage over time for 1.0M Strontium Electrolyte discharge. The graph plots cell voltage against time, with voltage values ranging from 0.0 to 2.5 V and time ranging from 0 to 120 minutes. The graph includes three lines: Cell Voltage, Calcium/Ref, and Carbon/Ref, with the latter two showing a lower voltage trend compared to the cell voltage.标注为：10 mA cm⁻² load.](image)
1.0M Strontium electrolyte saturated with sulphur dioxide

*Figure 6.9*
1.0M Sodium electrolyte discharge

Figure 6.10
As can be seen from table 6.1 three of the electrolyte systems, all showing cathode failure, have remarkably similar times on load to a two volt cut off point. These are balanced sulphur dioxide saturated, and 0.04M excess aluminium chloride calcium electrolytes, and balanced sulphur dioxide strontium tetrachloroaluminate. It would appear that after ~120 minutes at the applied load of 10 mA cm$^{-2}$ the cathode becomes choked with calcium chloride. The time taken to fully "pack" the cathode will depend on the electrolyte composition, crystal habit and in particular will be a characteristic of the carbon(s) used in the fabrication of the cathode. In all these cases (table 6.1) S.A.B. is employed and it would appear that it is reaching its maximum capacity at which point pore filling and passivation occurs. This may not necessarily correspond to full utilisation since the penetration depth is likely to be a function of pore size and tortuosity.

An alternative explanation for the variation in cathode failure time is that the electrolyte is breaking down under the load, or is reacting with either cell components or discharge products in some way. If this is the case then the cell could be effectively electrolyte limited causing a shut down in one or other of the electrodes. To test this one of the PTFE test cells was taken and the electrolyte chamber enlarged. This had the added benefit
that a larger separator paper could be used. The size of the electrodes was kept constant. Any problems concerned with internal shorting of the cell due to a spreading cathode could now be eliminated. Unfortunately there was no reference electrode in this cell, hence failure mode could not be ascribed. The cell was discharged with a balanced sulphur dioxide saturated calcium tetrachloroaluminate electrolyte, and with balanced strontium tetrachloroaluminate both with and without sulphur dioxide. The results show that the extra electrolyte exerted no appreciable effect on the discharge performance. Thus proving that the 120 minute discharge limit was, as expected, not due to the electrolyte. Attention was therefore focused on the carbon electrode.

If the 120 minute on load time resulted from blocking of the carbon pores then a simple means to enhanced performance would be to use a higher internal surface area carbon black. More calcium chloride could then be accommodated in the carbon and the on load times would consequently be higher. All the discharges so far had utilised the same carbon namely a Shawinigan Acetylene Black (S.A.B.) cathode. This was chosen since it has excellent mechanical properties allowing ease of formation into thin cathodes with the addition of only 5% (by weight) of a PTFE binder. To test the above hypothesis a second type of carbon cathode employing Ketchjen Black EC DJ600 was prepared similarly containing 5% PTFE. This carbon was then mixed
with the former in the ratio of 1:19, DJ600:SAB. This equates to 95% SAB and 5% DJ600. Using a mixture of a low and high surface area carbon was deemed to be most suitable in that the DJ600 was much more fragile to handle. In addition when the cell (figure 6.1) was wetted up the carbon, if containing a higher proportion of DJ600, would flow under the pressure exerted by the bolts in the cell. In this way the carbon expanded around the separator paper causing an internal short circuit. This could have proved hazardous in a lithium anoded system with the build up heat and a potential molten anode. However in a calcium system the only noticeable difference was that the performance of the cell was considerably diminished. Mixing the carbons gave the best of both worlds, in that the mechanical integrity of SAB was retained and at the same time a higher surface area of the carbon was achieved. Although the carbon flowing problem was alleviated with this mixed carbon it was not altogether eliminated. As a consequence a number of cells were subject to premature failure due to carbon shorting. Using the larger electrolyte volume cell this problem was overcome. Cathodes of DJ600 without any SAB were tried in this cell but the flowing was too great and cell shorting resulted.

A cell was prepared utilising this 1:19 carbon and containing a balanced sulphur dioxide saturated electrolyte (one of the ~120 minute limited systems). Under the same load and in the same cell as used before this cell realised a performance of 148 minutes to two volts. Initial three
electrode measurements (i.e. utilising a reference electrode) indicated that the cell was still carbon limited. Further work was carried out with the larger electrolyte volume cell which had no reference electrode. A typical trace from this cell is shown in fig 6.11.

Three electrode measurements of a balanced electrolyte using the higher surface area (DJ 600 containing) carbon black gave an increase in performance to 118 minutes to 2V. The discharge is shown graphically in Fig 6.12.

Figures 6.11 and 6.12 support the view that increasing the discharge product capacity of the carbon cathode is crucial in maximising the output from a calcium anoded, thionyl chloride cell.
1.0M Balanced calcium electrolyte Sulphur dioxide saturated +5% DJ600 Carbon.

Figure 6.11
1.0M Calcium electrolyte with 5% DJ 600 in the cathode.

Figure 6.12
Chapter 7

Linear Sweep Voltammetry

The Technique

Linear Sweep Voltammetry is much used to examine unfamiliar electrochemical systems. In essence the technique is concerned with monitoring the current response of a system subject to a linear sweep of the electrode potential at a constant rate. Linear sweep voltammetry involves sweeping the electrode potential between two limits and then halting the sweep. A more widely used technique is that of Cyclic Voltammetry where upon reaching the upper limit of a linear sweep, the sweep is reversed either back to the original potential or to some new potential. As the sweep rate is known then the potential axis is also a time axis. The sweep rates for a cyclic voltammetric study of an electrochemical system can be varied between a few mV s\(^{-1}\) up to a few hundred V s\(^{-1}\). Higher rates can be used but other factors, in particular double layer charging become significant which limits the applicability of the results. The recording of the voltammogram is most conveniently carried out using an X-Y chart recorder. If the sweep rate is above about 500mV s\(^{-1}\) then the slew rate of the recorder will lead to a distortion of the voltammogram. In these cases the trace can be recorded another way, such as a microcomputer or an oscilloscope.
For the calcium thionyl chloride couple voltammetry was initially performed on a static system but it was soon shown to be necessary to use a rotating disc electrode, to obtain reproducible results when the system was swept anodically, i.e. under discharging, actively corroding conditions.

**The Rotating Disc Electrode**

In an electrochemical system concentration gradients always develop in a boundary layer, in contact with the electrode surface. By using a Rotating Disc Electrode (RDE) convection (defined as the transport of species brought about by an external mechanical force), is superimposed onto the normal diffusion process found due to the concentration gradient. Convection is in itself an important form of mass transport, current densities many times those limited by diffusion alone can be obtained in certain systems.

When the disc is rotated in a large volume of electrolyte it acts as a centrifugal pump, drawing the solution vertically upwards and then throwing it outwards.

Under normal circumstances at low overpotentials classical electrochemical systems observe behaviour as defined by the Tafel equation. Moving to greater overpotentials results in a restriction in the passage of current, due to the superposition of diffusion control. Steady state measurement of a classical system results in an initial exponential rise in the current response followed by a gradual tail to a diffusion limiting plateau. If the measurements are performed at a faster sweep rate (i.e. non
steady state) then a current peak will be observed before the diffusion limitation is established. In a passivating system once the isolating reaction product has grown then the electrode will undergo a transition from active to passive and the current will fall to zero.

When the electrode substrate material itself takes part in the reaction then the reaction rate will be changed considerably, particularly when the reaction product is insoluble and insulating. The film in the case of calcium batteries is not intact, the nature of the film growth results in a voluminous structure in which there is an equilibrium between growth and loss. This type of system is not typical and cannot be defined by the normal classical behaviour either at steady state or a transient state as would be encountered at higher sweep rates. The calcium tetrachloroaluminate thionyl chloride system produces a poorly defined non adherent film, which although not very soluble can still be attacked by the electrolyte resulting in the pitting as seen with the SEM (chapter 9). In conjunction with this, products will be escaping from the calcium electrode which will cause a disruption of the normal diffusion profile. Thus there is no classical exponential lift away from the equilibrium potential and a later plateau, or simple passivation due to the growth of a new insulating film.

The bulk concentration of electroactive species is situated at a distance from the electrode surface. This distance is determined by the boundary layer in which the
concentration is depleted by reaction with the electrode. In a diffusion limited system the concentration at the electrode surface is zero since the charge transfer can operate at such a rate so as to oxidise or reduce any species as soon as it arrives at the electrode surface. The depletion within the boundary layer results in a concentration gradient between the bulk electrolyte and the electrode. The magnitude of this gradient is thus controlled by either the bulk concentration or alternatively by the thickness of the diffusion layer. If the diffusion layer thickness is held constant (by means of a RDE) then the rate depends on the bulk concentration. This is a result of Fick's second law which shows that current is proportional to the rate of change of concentration with the distance from the electrode (i.e., $\delta C/\delta x$). Hence the steeper the concentration gradient the greater will be the rate. Increasing the bulk concentration or alternatively reducing the thickness of the boundary layer will affect the concentration gradient. This explains why the classically experienced diffusion limiting plateau in a voltammogram is dependent on the concentration of the bulk solution. Using a RDE the concentration gradient can be varied whilst the bulk concentration is held constant. This is achieved by altering the rotation speed since a faster rotation speed will result in a thinner boundary layer and consequently steeper concentration gradient.

A calcium electrode is actively corroding so that parts
of the film will periodically detach causing congestion about the electrode. The diffusion layer is particularly indistinct because of the insoluble porous structure present on the anode surface. Rotating the electrode is believed to impose a more rigorous diffusion layer which is less likely to be perturbed by the corrosion products from the calcium electrode. Calcium is being released from the anode producing calcium chloride. It is difficult to predict how far the calcium can get out into the diffusion layer before precipitating. Hence classical "hydrodynamic" data is not obtainable from extrapolation of LeVich data. This explains why only one rotation speed was used extensively. Measurements with an increased rotation speed indicated that the process was dominated by the movement of charge carriers through a reaction product film, evidenced as an ohmic limitation.

Experimental

The experimental set up comprised a Thompson Ministat and associated DRG16 ramp generator and a X Y chart recorder. The Y deflection recorded the current from the cell as a potential drop across a 10 Ω resistor in series with the counter electrode. (Resistor true value = 9.92 Ω). The X deflection was measured across the output terminals of the ramp generator.

Initial experiments were performed on a static system and using an electrolyte saturated with calcium chloride. As stated previously reproducible results were hard to obtain. This was particularly the case when the cell was swept in
the anodic direction. Sweeping in a cathodic direction gave a much better degree of reproducibility revealing that the current response was very small. This is as would be expected since the calcium cell acts as an electrochemical diode in resisting charging. All that was evident from the cathodic sweeps were peaks that were attributed to the electrolyte components.

Open circuit potentials were measured using a rotating disc calcium anode at a constant rotation speed of 600 r.p.m. All cells were assembled inside a dry air glove box ( <30 p.p.m. water). The rotating disc drive assembly was external to the dry box and electrical contact was achieved via a shaft and a compression spring connection (figure 7.1). A gas tight carbon gland surrounding the shaft prevented any wet air entering the glove box and at the same time stopped electrolyte fumes from escaping to the outside.

The test cell was designed with a calcium stud set into Teflon for an anode (figure 7.2). The calcium anode studs were prepared by polishing them using an abrasive paper to give a clean reproducible sample of calcium to test. The polishing regime first consisted of using 600 grade paper and then final polishing was achieved using 800 grade emery paper. The stud when set in teflon had a circular cross section with a diameter of 4mm. The reference electrode used was a silver/silver chloride which was brought into close contact with the anode by means of a Luggin capillary. The symmetrical counter electrode was a nickel disc.
Figure 7.1

Experimental Cell for Impedance and Cyclic Voltammetric Work.

Rotating Disc Electrode

Glove Box

Silver Reference Electrode

PTFE Shroud

Steel Shaft

Glass Cell

Spring Contact

Calcium Electrode

Counter Electrode
Working Electrode Design.

Figure 7.2

Steel Shaft

Grub Screw

Teflon Holder

Compression Spring

Calcium Electrode

Threaded Shroud
The electrolyte used to fill this test cell was 1.0 M calcium tetrachloroaluminate, in thionyl chloride. This electrolyte was either used as prepared or saturated with sulphur dioxide prior to use. Saturation at atmospheric pressure and room temperature was achieved at a level of 10 - 12% (v/v). The normal electrolyte could either be prepared in the way of Staniewicz (11), where an excess of calcium chloride is used relative to the amount of aluminium chloride present, or, alternatively by only adding enough calcium chloride to balance the Lewis acid. Both of these electrolytes were utilised and comparative studies were made.

Results and Discussion

Cyclic Voltammetry.

The open circuit potentials (OCP), of polished electrodes immersed in the four electrolyte compositions described above were measured in the same test cell relative to a silver/ silver chloride reference electrode. These results are in agreement with those of Peled (41) and Walker (42) in that the addition of sulphur dioxide leads to a marked increase in OCP. The values are presented in table 7.1.
Table 7.1

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>OCP / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;normal&quot; Ca(AlCl$_4$)$_2$</td>
<td>2.30</td>
</tr>
<tr>
<td>balanced Ca(AlCl$_4$)$_2$</td>
<td>2.37</td>
</tr>
<tr>
<td>&quot;normal&quot; Ca(AlCl$_4$)$_2$, SO$_2$ sat.</td>
<td>2.37</td>
</tr>
<tr>
<td>balanced Ca(AlCl$_4$)$_2$, SO$_2$ sat.</td>
<td>2.43</td>
</tr>
</tbody>
</table>

When the cells were left at open circuit OCP was seen to slowly increase over a number of hours. This again confirms previous work by Staniewicz (11). The negative shift in the open circuit potential of electrodes in a saturated electrolyte would tend to indicate that sulphur dioxide produced by corrosive decomposition of thionyl chloride is being retained in the corrosion product layer.

The results of cyclic voltammetric investigations are presented in figs 7.3 - 7.10. Typical reproducible behaviour was obtained after 30 minutes at the open circuit potential. This allowed the cell sufficient time to form an SEI with some degree of order and hence establish and maintain a dynamic equilibrium with the electrolyte. An SEI is formed on the calcium anode as soon as the electrode is placed into the tetrachloroaluminate electrolyte, but initially this is poorly formed and unevenly distributed. Calcium metal is known to form a protective layer of calcium oxide even in dry air and when first placed into the electrolyte this layer is gradually replaced with calcium.
1.0M Electrolyte saturated with Calcium chloride after 30 mins at open circuit.

\[ R = \frac{U}{i} \]

\( \frac{200}{20} \)
1.0M Calcium Chloride saturated Electrolyte after 2 hours at open circuit.

*Figure 7.4*
1.0M Electrolyte saturated both with Calcium chloride and Sulphur Dioxide after 30mins at open circuit.

Figure 7.5
1.0M Electrolyte saturated both with Sulphur Dioxide and Calcium chloride after 2 hours at open circuit.

Figure 7.6

![Graph showing the relationship between Current (1 mA) and Voltage (mV)]
1.0M Balanced Electrolyte after 30 mins at open circuit

Figure 7.7
1.0M Balanced Electrolyte after 2 hours at open circuit

Figure 7.8
1.0M Balanced Electrolyte Sulphur Dioxide saturated after 30 mins at open circuit.

*Figure 7.9*
1.0M Balanced Electrolyte Sulphur Dioxide saturated after 2 hours at open circuit.

Figure 7.10
chloride due to electrolyte attack.

All cyclic voltammograms shown represent a 700 mV anodic excursion. Polarisation to higher potentials simply extends the response with no further complicating detail becoming evident. On first inspection the balanced and calcium chloride saturated electrolytes show very little difference in their behaviour. What is evident however is that at low overpotentials the saturated electrolyte, exhibits a short induction period where the current is initially zero. Such an induction period is not seen with a balanced electrolyte. This would tend to indicate that an energy barrier to the passage of current exists which is analogous to the voltage delay phenomena generally observed in the operation of lithium oxyhalide cells. This is undoubtedly a characteristic of SEI electrodes and is probably related to the morphology of the layer itself. This, in turn, determines the ionic mobility within the SEI and the ease with which ions traverse the SEI / electrolyte interphase. There is no plateau limiting current that would suggest that mass transport is the ultimate controlling process. Rather, the current appears to be limited by the resistance of the film which covers the calcium anode. This resistance is constant, as is evidenced by the straight line response. This resistive phenomenon controls the current at overpotentials above 150 mV. In the case of the sulphur dioxide saturated electrolyte it can be seen that there is no "loop" at lower overpotentials and the trace does not apparently attain a constant resistance value until
the anodic polarisation exceeds 600 mV. Below this value the graph is a smooth curve which suggests that the presence of sulphur dioxide can promote SEI rearrangement whilst the electrode is active. The traces presented in figs 7.3 - 7.10 were all recorded at a disc rotation speed of 600 r.p.m. Further experiments were carried out at higher rotation speeds the resulting traces showed all the systems to be rotation speed independent. Thus reinforcing the conclusion that mass transport plays no part in the rate controlling process. The sweep speed was also varied between 10 mV per s, and 1 mV per s. Again no difference was observed, which emphasises in particular, the constant electrical resistance presented by the SEI layer. The slope (1/R) of the linear portion of the voltammogram was found to be independent of the Luggin tip to working electrode gap and hence not influenced by the electrolyte conductivity. There will of course be a resistive element due to the electrolyte, but the fact that the slope was independent of the gap indicates that this element is much smaller than the film resistance and thus is masked.

Since the OCP was seen to shift with time further experiments were carried out after being allowed to stand for 2 hours at open circuit before sweeping. The calcium electrode was rotated at a constant speed throughout the open circuit period.

The results of these traces for a balanced electrolyte both with and without sulphur dioxide, were identical to
those obtained after a 30 minute period at open circuit figs 7.7, 7.8 and 7.9, 7.10. The straight line portion of the graph was again observed beyond 600 mV overpotential for a sulphur dioxide saturated cell and 150 mV for a balanced non sulphur dioxide cell.

The results for calcium chloride saturated electrolytes however show considerable differences in behaviour with respect to the time at open circuit. The results of these experiments are given in figs 7.3, 7.4 and 7.5, 7.6. With a saturated calcium chloride, saturated sulphur dioxide electrolyte the "closed" shape seen before with a sulphur dioxide balanced cell is again seen. However in the former case there is a great reduction in the current response to the same over potential supplied. This indicates that the resistance of the film must be increasing since a greater potential difference is required to illicit the same current response. For example a current represented by a 50 mV deflection of the Y axis (i.e. corresponding to a current of 5 mA, or 2.5 mA cm⁻² ) requires an over potential of 175 mV after standing at open circuit for 30 minutes. After 2 hours at open circuit, the same current response can only be achieved at an over potential of 550 mV.

With a saturated calcium chloride non sulphur dioxide electrolyte 2 major differences are observed.

First, it can be seen that the induction period is extended and an anodic polarisation of -75 mV is required before current will flow. The second and major difference is
that the anode undergoes a passivation process at an overpotential greater than 500 mV (26 mA cm\(^{-2}\) of anode area). This would appear to occur since as the electrolyte is already saturated with calcium chloride then further calcium chloride formed by the corrosion reaction cannot be accommodated in the electrolyte. Thus the protective film will build up with time since it can only be reduced in size by a physical exfoliation of the film away from the calcium anode. This explains the increased induction period since a higher over potential is required to make the chloride ions cross from the solution to the calcium anode. In addition there is a limiting current when no more chloride ions can cross the SEI at a rate necessary to maintain the current. As current is drawn the SEI will further thicken and this leads to the anode passivation observed. The current spike seen when the anode has passivated can be explained since the film may crack allowing chloride ions to reach the anode. Repassivation occurs when the produced calcium chloride fills the crack and prevents more chloride reaching the anode by this "short cut". Current can again pass only when the potential difference becomes less and consequently the required rate of chloride ions at the anode also drops.

The increased induction period has also been shown by repetitive anodic sweeps, these result in a progressive elongation of the induction time. Sweeping the cell anodically will cause a rapid increase in the thickness of the surface film because the produced SEI cannot be taken
into the electrolyte. Thus the resistance of the film will increase and this will lead to the observed extended induction period.
Chapter 8

Faradaic Impedance Measurements.

Introduction

The electrode-electrolyte interphase can be studied using the technique of a.c. impedance. This can be used to elucidate complex reactions involving specific adsorption of reactants and products on the electrode surface.

In simple terms this method can be described as follows. A small amplitude sinusoidal potential perturbation is applied to an electrode which can, if required, be superimposed on to a d.c. polarisation. The frequency of the a.c. signal is varied and the way that the system responds to the perturbation is measured in terms of phase and amplitude changes.

A.C. Theory

Some of the laws underlying a.c. theory are outlined below. The alternating voltage at time $t$ is given by

$$V = V_{\text{max}} \sin (wt)$$

Using Ohms law this gives

$$I = \left[ \frac{V_{\text{max}}}{R} \right] \sin (wt)$$

where $V_{\text{max}}$ is the amplitude of the alternating voltage, $R$ the resistance and $w$ is the angular frequency ($2\pi F$). The resulting current may be expressed in terms of $I_{\text{max}}$, the amplitude of the alternating current, giving rise to the
following

\[ I = I_{\text{max}} \sin (wt') \]

\( t \) and \( t' \) in the above represent the time that has elapsed since the voltage and the current respectively passed zero on the alternating voltage/current sinusoid in a positive direction. The phase angle, between the current and voltage, is expressed as \( \phi \) then

\[ \phi = wt' - wt \]

and

\[ I = I_{\text{max}} \sin (wt - \phi) \]

The impedance of the cell (defined as \( Z \)) can be written in vector form:

\[
Z = \frac{V_{\text{max}}}{I_{\text{max}}} \arg \phi
\]

\[ = |Z| \arg \phi \]

Now the impedance can be defined as a vector of modulus \( |Z| \) and argument \( \phi \), the phase angle. The results can be shown in a complex plane plot where \( Z' \) the reactance (or imaginary component) is plotted against \( Z' \), the resistance (or real component). The complex impedance can thus be split into its real and imaginary parts and this can be expressed as shown below

\[ Z = Z' + jZ'' \]

where:

\[ Z' = |Z| \cos \phi \]

\[ Z'' = |Z| \sin \phi \]

and \( j = \sqrt{-1} \)
If the phase angle, $\phi$, is negative, the current will lead the voltage and the reactance can be represented by capacitors. On the other hand, if the phase angle is positive then the converse will be true, namely the voltage will lead the current and the reactance is inductive.

In electrode impedance, the former is most common, and it is conventional to represent capacitive reactances in the first quadrant of a complex plane plot, the inductive component lies beneath the axis. The values of $Z'$ and $Z''$ are dependent upon the frequency since the phase angle, $\phi$, will vary with changes in the angular frequency, $\omega$.

**Extension of Impedance Theory**

The simplest representation of an electrochemical system in terms of analogue circuit components is the series-parallel combination known as the Randles circuit (figure 8.2). This equivalent circuit comprises four elements, $R_n$ represents the ohmic resistance of the electrolyte solution (which also includes the metal leads to the electrodes). $C_{dl}$ is the double layer capacitance which varies with the d.c. potential and is dependent upon the nature of the electrolyte. $\Theta$ is the charge transfer resistance which represents the activation polarisation of the electrode reaction. The final component of this equivalent circuit is the Warburg impedance (W) which is the a.c. impedance due to charged species diffusing towards, or away from the electrode. However in many instances with real systems this does not adequately model the electrode
Figure 8.2 Randles Equivalent Circuit.

\[ R_{\text{n}} + C_{\text{dl}} = W \]
behaviour. It is general practice to modify, usually by addition of other components, the equivalent circuit to obtain a more faithful model. These additional components have been used to represent the action of adsorbed species on the surface of the electrode (43, 44 & 45). Complex reactions involving adsorbed and soluble intermediates and reactions with electrolyte dissolution, deposition and active-passive transition have also been studied by using an impedance technique. Reviews of typical systems are provided by Armstrong (46) and MacDonald (47).

Porous electrodes were first considered by de Levie (48 - 50). Hampson et. al. (51) suggested that for electrodes exhibiting a surface roughness, a factor, $\tau$, should be used. This factor can range between 1 for a perfectly smooth electrode, down to 0.5 for an electrode which is roughened to such an extent so as to be to all intents and purposes, porous. This treatment arises from the work on porous electrodes by de Levie (50) who concluded that:

a) the phase angle of the impedance of a porous electrode is half that of an equivalent planar electrode, so that for a perfect system this angle will be 22.5°.

b) the absolute magnitude of the impedance of a porous electrode is proportional to the square root of that of the equivalent flat electrode.

The graph of $Z = Z' + Z''$ shows a series of points at different frequencies, at low frequencies the impedance becomes purely resistive because the reactance of the
The impedance spectra were measured using a 3 electrode cell similar to that used for the cyclic voltammetric study (chapter 7 fig 7.1). The three electrode cell was connected via a solartron 1186 electrochemical interface to a solartron 1250 frequency response analyser. The data was collected, and the analyser controlled by a Kemitron K3000 micro computer. A schematic diagram of the experimental apparatus is shown in figure 8.1.

Single frequency measurements showed that the most suitable sense resistor was 100 n. The integration time was set to 10 seconds in order to allow a number of full cycles at the lower frequencies.

Results and Discussion

No equivalent circuit will be proposed for the calcium system in this thesis. This is for two reasons, the first is that the complexity of the system makes it very difficult to suggest an unambiguous model that fits the experimental data well enough. The second reason arises after consideration of a paper by MacDonald (47) who reinforces the belief that the analogy between a corroding interface and an equivalent electrical circuit cannot be taken too far. He quotes an example of negative resistance which can predicted from reaction mechanism theory, cannot be accounted for by an electrical analogue composed of passive elements. Likewise,
Schematic Design of Impedance Apparatus.

Figure 8.1
"pseudo-inductance" does not imply that an inductor physically exists at the interface but merely that the imaginary component of the reaction impedance is negative. Also by its nature any equivalent circuit of an actively corroding system can only be accurate if considered as a snapshot in time. As the corrosion continues the values of resistors and capacitors will change and the model will no longer be accurate.

The four electrolytes that have been surveyed for the impedance study are the same as those used for the cyclic voltammetric work (chapter 7), namely balanced, calcium chloride saturated and the sulphur dioxide saturated variants of these two. The impedance traces are taken at open circuit after 5 minutes, 30 minutes, 2 hours and 16 hours for each electrolyte at open circuit. The on load traces were after 2 hours at open circuit and measured at an anodic polarisation of 200 mV. The open circuit times were chosen so that the process of SEI growth could be monitored, and corrosion data obtained at times less than that possible using the weight loss data in chapter 4.

The results are shown in figs 8.3 to 8.22. The figures are summarised in table 8.1. As can be seen the same basic shape for the impedance trace is maintained by all the electrolytes, there are however significant differences between the respective electrolyte types. There are general trends that are constant to all of the electrolytes, such as the size of the semi-circle diminishes when the cell is
placed on load. This is as would be expected since the protecting film will be diminished in thickness when the cell is placed on load. This will result in a reduction of the resistance (or impedance) of the film and consequently explain the smaller semi-circle seen in the impedance trace. The traces do not show any typical Warburg diffusion element, which would suggest that the process is not diffusion controlled in the normal sense. This is again in agreement with other results, particularly the cyclic voltammetric data (chapter 7) in which there is no current limited plateau. This was checked by changing the rotation speed of the electrode. The traces proved to be rotation speed independent.

Figs 8.3 to 8.7 show a cell containing the calcium chloride saturated electrolyte. In general the size of the impedance traces are much smaller than those shown of the other three electrolyte systems. This suggests that the film resistance is smaller and hence the protection afforded by the film on the calcium anode is less. Consequently the rate of corrosion will be higher.
<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Electrolyte</th>
<th>Time before sweeping</th>
<th>Notes</th>
</tr>
</thead>
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<tr>
<td>8.3</td>
<td>CaCl$_2$ sat</td>
<td>5 mins</td>
<td></td>
</tr>
<tr>
<td>8.4</td>
<td>dto</td>
<td>30 mins</td>
<td></td>
</tr>
<tr>
<td>8.5</td>
<td>dto</td>
<td>2 hours</td>
<td></td>
</tr>
<tr>
<td>8.6</td>
<td>dto</td>
<td>16 hours</td>
<td></td>
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<td>8.7</td>
<td>dto</td>
<td>2 hours</td>
<td>200 mV on load</td>
</tr>
<tr>
<td>8.8</td>
<td>CaCl$_2$, SO$_2$ sat</td>
<td>5 mins</td>
<td></td>
</tr>
<tr>
<td>8.9</td>
<td>dto</td>
<td>30 mins</td>
<td></td>
</tr>
<tr>
<td>8.10</td>
<td>dto</td>
<td>2 hours</td>
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<td>dto</td>
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<td>2 hours</td>
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</tr>
<tr>
<td>8.14</td>
<td>dto</td>
<td>30 mins</td>
<td></td>
</tr>
<tr>
<td>8.15</td>
<td>dto</td>
<td>2 hours</td>
<td></td>
</tr>
<tr>
<td>8.16</td>
<td>dto</td>
<td>16 hours</td>
<td></td>
</tr>
<tr>
<td>8.17</td>
<td>dto</td>
<td>2 hours</td>
<td>200 mV on load</td>
</tr>
<tr>
<td>8.18</td>
<td>Balanced SO$_2$ sat</td>
<td>5 mins</td>
<td></td>
</tr>
<tr>
<td>8.19</td>
<td>dto</td>
<td>30 mins</td>
<td></td>
</tr>
<tr>
<td>8.20</td>
<td>dto</td>
<td>2 hours</td>
<td></td>
</tr>
<tr>
<td>8.21</td>
<td>dto</td>
<td>16 hours</td>
<td></td>
</tr>
<tr>
<td>8.22</td>
<td>dto</td>
<td>2 hours</td>
<td>200 mV on load</td>
</tr>
</tbody>
</table>

With the passage of time, the size of the semi-circle...
Figure 8.4
Figure 8.5
Figure 8.6

The figure shows a graph with the real part of Ohms on the x-axis, labeled "Real Ohms (Thousands)" and the imaginary part of Ohms on the y-axis, labeled "Imaginary Ohms (Thousands)". The graph includes a curve and marks indicating certain frequencies such as 800 Hz and 1.6 MHz.
Figure 8.7
Figure 8.9
Figure 8.11
Figure 8.12
Figure 8.13
Figure 8.15
Figure 8.19

![Diagram](image)
Figure 8.21

Rea./Ohms (Thousands)

Imag./Ohms (Thousands)

60 Hz

(Thousands)

Real/Ohms
Figure 8.22
increases. This is as would be expected since the film will thicken as corrosion progresses. As the film thickens greater protection of the calcium anode will result and the rate of corrosion will fall. This has already been evidenced by the weight loss graph (chapter 4), which shows a decrease in the rate of corrosion with the progression of time.

The other three electrolyte systems that were surveyed exhibited a different impedance pattern (figs 8.8 - 8.22). Firstly the sizes of the semi-circles are all larger, in some cases much larger, suggesting that the corrosion protection is greater. With these three electrolyte systems the simple trend of a gradual increase in the size of the semi-circle is not observed. Hence corrosion protection is not purely a matter of increasing film thickness due to the corrosion of the calcium anode. After 5 minutes at open circuit the film exhibits a higher resistance because the SEI layer is ordered, the translucent contact film seen in the SEM study (chapter 9) is probably controlling the process. After 2 hours at OCP the layer is becoming disordered and the semicircle is smaller. Some of the original SEI will be lost due to dissolution. i.e. initially the translucent layer will be virtually intact, yet after 2 hours the film will have developed more faults so that the resistance will be diminished.

The solubility of calcium chloride in these electrolytes gives rise initially to a more uniform protective film since a process of dissolution and
reprecipitation can take place. With a CaCl₂ saturated electrolyte there is no capacity for any more calcium chloride to be taken into the electrolyte and so the initial film is unable to reorganise to form a more uniform and cohesive layer. The calcium chloride will be precipitated wherever the chloride ions meet calcium ions hence there will be a distribution of crystal sizes and the corrosion layer surface is likely to be incomplete, or porous in nature.

The CaCl₂ saturated electrolyte impedance traces start at their smallest after 5 minutes (fig 8.8) which suggests that this system has already gone through the resistance maximum seen with the other electrolyte types.

It is possible therefore that this technique can thus be used to screen electrolytes for their corrosive nature. Thus eliminating the need for three month weight loss corrosion studies. A smaller semicircle implies a smaller film resistance and greater film porosity leading to greater attack by the electrolyte and consequently less corrosion resistance. The converse is true of a large semicircle.

On load impedance behaviour is difficult to quantify but the semi-circles for all of the electrolytes decrease in size, as would be expected as the film is reduced in thickness due to the active dissolution of the calcium anode.

Summary

As can be seen in chapter 4 reproducible weight loss
data was not obtained at times under around 50 hours of open circuit corrosion. The impedance study was undertaken to elucidate the corrosion process at times under 50 hours. The recorded data suggests why the corrosion results were irreproducible at shorter times, in that there is a process of stabilisation of the anode as the initial translucent film is attacked by the electrolyte and a dynamic equilibrium is established between the dissolution and precipitation of the protecting calcium chloride SEI film.

Of the four electrolytes surveyed the one that gives the best corrosion protection appears to be the system saturated both with calcium chloride and then with sulphur dioxide.
Chapter 9

SEM analysis of Calcium Anodes

To complement the electrochemical experiments, samples have been taken throughout for analysis using the scanning electron microscope (SEM) facility at the Alcan labs, Banbury. These micrographs have been used to back up ideas formed from other electrochemical techniques, specifically the corrosion studies, and the cyclic voltammetric work. The micrographs provide physical evidence that the SEI films formed in the various electrolytes are different in structure and that the degree of corrosion varies from one electrolyte type to another.

The micrographs were taken using a Jeol 300 machine. The accelerating voltage used was 20 kV.

Corrosion Studies

Calcium samples that had received the same pretreatment as those for the discharge studies (chapter 6) were taken and placed in either a normal 1.0M electrolyte or one that had been saturated with sulphur dioxide at atmospheric pressure. The calcium samples were in the form of discs which had been polished and then cut in two. One half of each of the discs was placed in the normal electrolyte and the other half in a sulphur dioxide containing electrolyte. The samples were periodically visually inspected at times up
to 24 hours. The results were encouraging in that the sulphur dioxide containing samples seemed to be noticeably less affected by the electrolyte than the normal electrolyte samples. It was thus decided to undertake a more quantitative study, run in parallel with the weight loss experiments (chapter 4), in order to monitor the open circuit corrosion using a scanning electron microscope.

**Experimental**

Discs were punched out from the calcium foil (New Met) and then mechanically polished using abrasive discs. The calcium sample was held in a perspex holder and the abrasive disc was lubricated using the polishing oil (detailed in chapter 3). They were subsequently degreased using dry acetone prior to use. The discs were placed in sealed sample containers with either a normal 1.0M electrolyte or one saturated with sulphur dioxide. Periodically discs were removed, dried and then stored in an electrolyte free glove box (to eliminate the possibility of any further corrosion) prior to SEM evaluation.

**Results**

After 48 hours the sample not containing sulphur dioxide showed a blistering across the surface of the disc. The sulphur dioxide sample, after the same time, has a much cleaner appearance showing isolated sites of corrosion. The differences between the two electrolyte samples become more pronounced with the passage of time figures 9.5 through to 9.10. The SEM investigation was maintained for the duration
of the corrosion experiments (i.e. 3 months). The black bar in the lower right hand corner of the micrograph denotes the number of microns shown below it (for 1000 x's this is 10). The next number gives the accelerating voltage in kV, and the last two refer to the film and frame number respectively. Table 9.1 gives an index to the chosen micrographs which are typical of the surface of the calcium samples. They allow the pattern of corrosion to be followed in both electrolytes.

The first four of the micrographs show calcium samples after 48 hours of corrosion. These four are taken at 500 x's magnification. Figs 9.1 and 9.2 depict a sample corroded in a normal electrolyte, even at this very short time it is evident that the corrosive attack is very aggressive. Figs 9.3 and 9.4 show samples exposed to an electrolyte saturated with sulphur dioxide. Fig 9.3 shows the local corrosion that has occurred. The sites of corrosion are isolated the vast majority of the surface is represented by fig 9.4. It is interesting to note that the calcium sample is virtually untouched, the scratches on the surface are the original polishing marks remaining after sample preparation.
<table>
<thead>
<tr>
<th>Figure no.</th>
<th>Electrolyte</th>
<th>Time of Corrosion /hours.</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>No SO₂</td>
<td>48</td>
<td>Local blistering</td>
</tr>
<tr>
<td>9.2</td>
<td>No SO₂</td>
<td>48</td>
<td>Majority of surface</td>
</tr>
<tr>
<td>9.3</td>
<td>SO₂ sat.</td>
<td>48</td>
<td>Localised effect</td>
</tr>
<tr>
<td>9.4</td>
<td>SO₂ sat.</td>
<td>48</td>
<td>Majority of surface</td>
</tr>
<tr>
<td>9.5</td>
<td>No SO₂</td>
<td>96</td>
<td>500 x</td>
</tr>
<tr>
<td>9.6</td>
<td>SO₂ sat.</td>
<td>96</td>
<td>2000 x</td>
</tr>
<tr>
<td>9.7</td>
<td>No SO₂</td>
<td>408</td>
<td>1000 x</td>
</tr>
<tr>
<td>9.8</td>
<td>SO₂ sat.</td>
<td>576</td>
<td>1000 x</td>
</tr>
<tr>
<td>9.9</td>
<td>No SO₂</td>
<td>2112</td>
<td>1000 x</td>
</tr>
<tr>
<td>9.10</td>
<td>SO₂ sat.</td>
<td>2112</td>
<td>1000 x</td>
</tr>
</tbody>
</table>

Figure 9.6 shows the corrosive action taking place in a sulphur dioxide environment after 96 hours at a magnification of 2000 x's. This localised corrosion is comparable to that seen over the whole surface of the non sulphur dioxide saturated sample (figure 9.5) at a magnification of only 500 x's, suggesting that the mode of corrosion is similar yet greatly decreased in rate.

The general progression in a sulphur dioxide containing
electrolyte, evident after 576 hours, (figure 9.8) is towards the production of a surface which is coraloid in nature. This is normally indicative of a recrystallisation process due to enhanced solubility of the corrosion product in the electrolyte. In contrast figure 9.7 shows the continued erosion of an actively corroding surface resulting in penetration of the sample and considerable undercutting.

The final effects of what appears to be due to differences in the initial corrosion product morphology and its subsequent solubility in the appropriate electrolyte are illustrated in figures 9.9 and 9.10.

The non sulphur dioxide sample is very badly pitted over the whole surface. There are a number of places where the corrosion has penetrated through the sample. The corrosion of the sulphur dioxide containing sample however, is far less, there are no holes in the sample and the surface film appears far more continuous, tenacious and protective.

**On-load Samples**

In addition to the open circuit study described above sample anodes from cells from which current had been drawn were also examined. The experimental set up for this was the same as that used for the cyclic voltammetry (fig7.1). These series of experiments were carried out to provide physical evidence for the change in surface layer expected from the voltammetric behaviour in different electrolytes reported in chapter 7.
Samples of calcium anodes that had been exposed to different electrolyte systems were taken for SEM analysis. Four electrolytes were surveyed, namely balanced, calcium chloride saturated and the sulphur dioxide saturated versions of these two. The anodes were allowed to remain at open circuit for two hours before being polarised. Throughout the experiment the electrodes were rotated at a constant 600 rpm. The samples were all swept 600mV anodically from their open circuit potentials. This value was chosen since the passivation seen in the voltammograms of a saturated electrolyte occurred at around 520mV (chapter 7). Hence for the saturated electrolyte this sample should already be passive. It was hoped that the surface morphology responsible for this phenomenon would be readily visible. In addition to the two hour samples, a further calcium chloride saturated electrolyte sample was taken after only a 30 minute stand at open circuit. After this shorter open circuit period the anode was not seen to passivate on subsequent polarisation. Therefore comparison could be made between electrodes taken to the same anodic overpotential resulting in both the passive and active state. The SEM was set up with an accelerating voltage of 20 kV. The magnification was kept constant at 1000 x's, the black bar seen on the photographs signifying 10 microns.

**Results**

The sample taken from a saturated electrolyte, that had only rested for 30 minutes at open circuit, was surveyed
first. The overall structure was similar to that already seen in a non sulphur dioxide electrolyte, open circuit corrosion, sample. Figure 9.11 shows a typical area, some regions exhibited a more pitted morphology but the sample was otherwise uniformly corroded. There is a translucent film, which appears to be very thin, on the surface of the sample. This film is common to most of the other electrolyte types, and a probable explanation for its presence is that it is the layer which initially formed when the calcium first makes contact with the electrolyte. This film will remain on the surface of a growing SEI layer because of the method by which the cell operates. In a calcium system it is the chloride ions that cross the SEI and the film is built up from the underlying calcium anode. (In a lithium system it is the lithium ions which are mobile and so the SEI is built up from the solution side. As such this initial layer will ultimately be hidden by lithium chloride formed by further corrosion of the lithium anode or when the cell is placed on load.)

The sample taken from a saturated calcium chloride electrolyte, that had been allowed to remain at open circuit for two hours before sweeping shows a very different morphology (an index of the figures is shown in table 9.2). Illustrated in figs 9.12, 9.13 and 9.14. The fact that the calcium anode has passivated is apparent from the general appearance of the surface. The general picture is represented by fig 9.12. This confirms a very different
structure to that seen after 30 minutes at open circuit. Here there are very few sites which show an open porous structure, and the dense "string" like layer effectively shuts down the reactivity of the electrode. It seems that the open area is covered by this new layer blocking the underlying pores preventing the electrolyte penetrating through to the anode substrate. It also appears that this new layer either envelopes or incorporates the translucent film. The presence of the thin translucent film could well explain the resistive nature of the electrode as recorded in cyclic voltammetry studies, in that it acts as a membrane limiting the rate at which chloride ions can pass through it. This effect dominates at higher overpotentials and so the typical Tafel and diffusion limiting behaviour is not observed.

The sample of a calcium chloride saturated electrolyte which has subsequently been saturated with sulphur dioxide is shown in figs 9.15 and 9.16. The surface is very uniform and consists of a great many pits across the anode. The surface appears to be tending towards the "spongy" type layer seen in the early stages of the open circuit corrosion studies, but this film does not form a cohesive layer. It has large holes blown in it since current is being continually drawn. At the bottom of the pits formed in the corrosion layer secondary pitting is occurring, if to a slightly lesser extent than that seen in fig 9.11. The translucent film is again present and covers most of the
surface. Its thickness is estimated to be around 0.1 microns.

The sample from a balanced electrolyte without sulphur dioxide shows a morphology of surface film which is similar to that seen for a calcium chloride saturated electrolyte. It is shown in figs 9.17, 9.18 and 9.19. The most typical area is that shown in fig 9.17 where the surface has large holes in the protecting corrosion product film. The translucent film seen previously is readily apparent and although the surface coverage is not complete it is of such an extent so as to be likely to influence the performance of the cell.

The final sample that has been examined is that exposed to a balanced electrolyte which was subsequently saturated with sulphur dioxide. The surface is shown in figs 9.20, 9.21 and 9.22. The "spongy" type of film seen in an unbalanced sulphur dioxide saturated electrolyte is again seen here. It appears to be better established and possibly more tenacious. Although there are some pits across the surface they do not seem to be as wide spread as in previous samples. Instead the film appears to crack. It is likely that the cracks are formed in the early stages of drying or as a consequence of the high vacuum present in the SEM. This idea is reinforced by the fact that there is an intimate match between both sides of the cracks and no "rounding" is apparent as might be expected if corrosion was playing a part. It is assumed therefore that these cracks do not play
any part in the operation of the cell.

Table 9.2

<table>
<thead>
<tr>
<th>Fig no.</th>
<th>Electrolyte</th>
<th>Time before sweeping / hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.11</td>
<td>CaCl₂ sat.</td>
<td>0.5</td>
</tr>
<tr>
<td>9.12</td>
<td>CaCl₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.13</td>
<td>CaCl₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.14</td>
<td>CaCl₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.15</td>
<td>CaCl₂,SO₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.16</td>
<td>CaCl₂,SO₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.17</td>
<td>Balanced</td>
<td>2</td>
</tr>
<tr>
<td>9.18</td>
<td>Balanced</td>
<td>2</td>
</tr>
<tr>
<td>9.19</td>
<td>Balanced</td>
<td>2</td>
</tr>
<tr>
<td>9.20</td>
<td>Balanced SO₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.21</td>
<td>Balanced SO₂ sat.</td>
<td>2</td>
</tr>
<tr>
<td>9.22</td>
<td>Balanced SO₂ sat.</td>
<td>2</td>
</tr>
</tbody>
</table>

Studies of the electrolyte alone

There is an obvious effect due to the addition of sulphur dioxide. The question still arises, however, is the modification of the corrosion layer a direct influence of sulphur dioxide at the surface or does the sulphur dioxide interact with the calcium tetrachloroaluminate in such a way so as to change the crystal morphology of the surface
layer. In order to try to answer this question calcium discs were exposed for a period of a week to the following three electrolyte systems.

1. Sulphur Dioxide only,
2. Thionyl Chloride only,
3. Thionyl Chloride saturated with Sulphur Dioxide.

After the corrosion period the samples were inspected visually. Sample 2 appeared brighter than the others exhibiting very little evidence of corrosion. This is in agreement with the work of Staniewicz (11). Sample 3 appeared bright with a number of specific sites of attack. These were seen as black flecks on the bright metallic background. The flecks were scattered uniformly across the entire surface of the disc. Sample 1 appeared to be 60 - 70% covered by a whitish deposit. The rest of the sample was a darker grey.

The sample discs were then prepared for SEM analysis by gold coating. The EDAX facility on the SEM was employed to try and ascertain the composition of the surface films. The figures are summarised in table 9.3. Figs 9.23, 9.24 and 9.25 are SEM's of the sample containing thionyl chloride only. Fig 9.25 is at a low magnification (50 x's) and indicates that the corrosion is limited to a small number of specific sites. Fig 9.23 represents a higher magnification (1000 x's) of one of these corroding areas. Fig 9.24 is at the same magnification showing the more typical area with very little corrosion in evidence. Figures 9.23a, 9.24a and
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Figure 9.23a

K alpha lines
Figure 9.24a

Link Systems Ltd X Ray Analysis

K alpha lines
9.25a are the respective EDAX traces. From the position of the K alpha lines they show that the corrosion product is calcium chloride, that the rest of the sample is almost exclusively calcium.

The sample that had been exposed to a thionyl chloride, sulphur dioxide saturated electrolyte is depicted by figs. 9.26, 9.27, 9.28, 9.29 and 9.30. Fig 9.30 is at a low magnification (50 x's) and shows the distribution of the corrosion sites. The large dark areas around some of the particles are shadows caused by blocking of the electron beam. This was verified by adjusting the tilt of the sample within the instrument causing the dark patches to disappear. Fig 9.26 shows a higher magnification (1000 x's) of the most typical area on the sample. Fig 9.29 is at the bottom of one of the very few pits, and fig 9.27 shows the top of one of the particles. Fig 9.28 is a slightly reduced magnification (500 x's) of the same particle shown by fig 9.27, showing more of the structure.

Figures 9.27a, 9.29a and 9.30a are EDAX traces of the respective SEM pictures. Fig 9.30a shows that again the predominant species is calcium and that some calcium chloride is present. Fig 9.29a shows that the corrosion sites are again principally calcium chloride, but that there is a measurable amount of a calcium sulphur containing species. This is more likely a calcium, sulphur, oxygen species but oxygen being such a light element is not easily detected by EDAX measurements. Fig 9.27a showing the composition at the top of a particle also shows a certain
Link Systems Ltd X Ray Analysis

Figure 9.27a
Link Systems Ltd X Ray Analysis

Figure 9.30a

K alpha lines
amount of sulphur. This would appear to be less than at the sites themselves. These results suggest that the main concentration of the sulphur containing corrosion product is at the base of the pits. The majority of the corrosion is due to calcium chloride formation.

The sample that had been exposed to sulphur dioxide only is depicted by figs 9.31, 9.32, 9.33 and 9.34. Fig 9.34 is a low magnification picture (50 x's). There are far more sites of corrosion than have been present in the other two samples. Figure 9.32 shows the corrosion product to be particulate in nature. Fig 9.31 shows a typical area the surface which appears to be solid with particles scattered over it. Fig 9.33 shows in more detail the structure of one of the particles that appears on the surface of the sample. Figures 9.31a and 9.33a are EDAX traces of the respective SEM pictures. Fig 9.31a is a representation of the non particulate part of the sample and indicates that the corrosion product detected is mainly a calcium sulphur species. The chloride can only be present as an impurity, presumably when the sample was removed from the electrolyte and exposed to the chloride present in the atmosphere of the glove box. Fig 9.33a portrays the composition of one of the particles. This has a higher relative intensity of elemental sulphur suggesting that there is less calcium oxide present in the particle.
Figure 9.31a
Link Systems Ltd X Ray Analysis

Figure 9.33a

K alpha lines
In addition to the EDAX traces samples have been analysed using an ESCA technique. This was performed on a sample from a balanced 1.0M electrolyte in order to ascertain the composition of the sulphur component. The sulphur binding energies (52) were measured at around 170 eV which suggested a highly oxidised species probably CaSO₄.

It is obvious that calcium is thermodynamically unstable in thionyl chloride but the formation of a tight passive corrosion product layer curtails any further attack.
except at localised defect sites within the film. It is also apparent that sulphur dioxide is aggressive towards calcium metal and that the corrosion product film is much less protective than that formed from calcium chloride.

A mixture of the two solvents behaves as if the system is controlled by the interaction of thionyl chloride with the metal, i.e. the calcium chloride layer protects the calcium surface from attack by sulphur dioxide yet at the points where access is made available to the underlying metal (film defects) some sulphur containing product is in evidence. Additionally there are some specific corrosion sites in the mixtures suggesting sulphur dioxide is facilitating attack at weak points in the calcium chloride film which would normally be resistant to thionyl chloride alone. These could be the thinner or stressed areas of the calcium chloride layer which is being selectively dissolved due to the presence of sulphur dioxide, adding credence to the observation that sulphur dioxide increases the solubility of calcium chloride.

**Induction period and near passive samples**

As stated previously from the cyclic voltammetric studies (see chapter 7), it was noted that the calcium anode passivated in a calcium chloride saturated electrolyte under anodic polarisation. These results showed that an anodic polarisation of $510 - 515$ mV was required to induce anode passivation. The shape of the voltammogram (fig 7.4) indicates that the passivation process is very fast since
the current drops immediately rather than plateauing and then tailing off. Samples of calcium anodes were polarised 505 mV anodically and then investigated using the electron microscope to identify the passivating process. Other samples were polarised 100 mV anodically for comparison. This was selected since it is greater than the induction potential where the current is essentially zero in a calcium chloride saturated electrolyte. The figures are summarised in table 9.4. Figs 9.35 to 9.37 show this 100 mV polarisation whilst figs 9.38 to 9.41 show the 505 mV polarisation.

Table 9.4

<table>
<thead>
<tr>
<th>Fig no.</th>
<th>Electrolyte</th>
<th>Magnification</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.35</td>
<td>CaCl₂ sat</td>
<td>500</td>
</tr>
<tr>
<td>9.36</td>
<td>CaCl₂ sat</td>
<td>1000</td>
</tr>
<tr>
<td>9.37</td>
<td>CaCl₂ sat</td>
<td>1000</td>
</tr>
<tr>
<td>9.38</td>
<td>CaCl₂ sat</td>
<td>500</td>
</tr>
<tr>
<td>9.39</td>
<td>CaCl₂ sat</td>
<td>350</td>
</tr>
<tr>
<td>9.40</td>
<td>CaCl₂ sat</td>
<td>500</td>
</tr>
<tr>
<td>9.41</td>
<td>CaCl₂ sat</td>
<td>1000</td>
</tr>
</tbody>
</table>

The 100 mV sample that had been stirred for 2 hours prior to sweeping showed none of the string like structure seen in a totally passivated electrode (fig 9.12). The sample showed a voluminous layer which was cracked showing extensive corrosion beneath the film surface. This layer covered approx 1/5 to 1/2 of the electrode area. Fig 9.35
shows a crack in the film magnified 500 x's, fig 9.36 is at a higher magnification, (1000 x's) of the cracked film and shows in better detail the corrosion occurring underneath. The voluminous layer would appear to be the structure that limits the current response during the induction period and the cracks in this and subsequent corrosion are evidence of current starting to flow. Fig 9.37 shows the part of the sample that is not covered by the layer, and would suggest that the protecting layer has been lost from this portion of the sample altogether. There are small pillars which would appear to be the remnants of the voluminous film suggesting that initially at least the coverage of this film is very good. This also fits in with the induction period seen on the voltammogram (fig 7.4), since if the film coverage was only around 50% then some current response would be seen at lower overpotentials (under 75 mV anodic polarisation).

For the samples polarised to 505 mV anodically the sample was very similar across its entire surface. It appears to consist of pillars of calcium with stretched and folded tops, surrounded by areas were the calcium has been corroded. There is no evidence of the voluminous layer at all suggesting that at these higher loads all of it has been lost. Fig 9.38 shows the folded like nature of the film supported by the calcium pillars (500 x's magnification). Fig 9.39 is at 350 x's magnification and shows the transition from the film to the corroding areas. On fig 9.39 careful inspection shows that detail is evident beneath the film. Since the accelerating voltage used on the microscope
was 20 kV this equates to around 1 micron penetration into the sample. Fig 9.40 shows another section of the folded layer this time magnified to 500 x's again detail beneath the film is evident. Fig 9.41 is at 1000 x's and of the corroded part between the areas of the folded film. The fuzzy white areas are likely to be pillars of calcium. The thin translucent film is also apparent on this picture (lower left hand corner) suggesting that the folded layer grows on top of this. These results would strongly appear to be a precursor of the string like structure seen on a totally passive electrode (fig 9.12). At 505 mV anodic polarisation the electrode is still active. It would appear that around this level of polarisation the calcium chloride produced becomes far in excess of that which can be readily lost to the electrolyte. Therefore since the electrolyte in this case has no excess capacity for calcium chloride, this is precipitated onto the calcium anode and leads very quickly to a thickening of the film to such an extent that the supply of chloride ions is choked off. This results in the anode passivation seen in the voltammetric study (chapter 7 fig 7.4).
Chapter 10

Discussion of results

This chapter attempts to consolidate the results presented during the experimental chapters (no.s 4 to 9) and to draw conclusions from the various sources of data.

There are a number of anomalies raised in the previous chapters, most notable of which is that sulphur dioxide addition to the electrolyte leads to both an increase in the solubility of the protecting calcium chloride layer and at the same time decreases the rate of open circuit corrosion. These apparent discrepancies are dealt with in this chapter.

Increases in cell performance

The most significant difference in the performance characteristics of the various cells that have been discharged is that some suffer from anode failure whilst others exhibit failure of the cathode. As a general rule those cells that suffer from cathode failure give a greater time on load. The anode failure can be explained as being due to calcium passivation because of the increased thickness of the porous part of the SEI. The film can build up during the cell operation and presents an ever increasing barrier to the passage of chloride ions. This effectively results in an isolation of the calcium anode from the
electrolyte and the failure of the cell. By contrast an electrolyte saturated with sulphur dioxide gives rise to a cathode failure, and affords an increased capacity of the cell. Cathode failure is observed in a cell containing a 1.0M sulphur dioxide saturated Calcium tetrachloroaluminate electrolyte and a Shawinigan Acetylene Black cathode. A balanced 1.0M calcium electrolyte results in cathode failure in a similar way to a sulphur dioxide saturated one. An electrolyte that contains an excess of aluminium chloride also gives rise to a cathodic failure. Adding sulphur dioxide to the electrolyte (or operating the cell with an excess of aluminium chloride) increases the solubility of calcium chloride in the electrolyte. This excess solubility has been measured (chapter 5) by means of atomic absorption and found to be $3.3 \times 10^{-3}$ M for a sulphur dioxide saturated electrolyte.

The excess solubility of calcium chloride in the electrolyte allows the reaction products to dissolve away from the anode. The largest concentration of chloride ions will be at the cathode where thionyl chloride is reduced to form sulphur dioxide and chloride ions. If calcium ions can be taken into the electrolyte then they will migrate towards the cathode, preferentially forming calcium chloride there. This will lead to the blocking of the pores within the carbon matrix and to premature failure of the cathode. The higher the solubility, the more efficient this transport should be, which will lead to greater penetration into the
carbon. Thus better carbon utilisation is achieved and longer discharge times together with greater cell capacity are available. That solubility of calcium chloride can be seen to be the key to increased cell performance is illustrated by the discharges of cells that are saturated with both calcium chloride and sulphur dioxide. Increased cell performance results if the electrolyte is saturated first with calcium chloride. If the electrolyte is saturated with sulphur dioxide first then subsequent saturation with calcium chloride will overcome any increased capacity for calcium chloride. If the increased cell performance was due to film doping then the order of saturation would not affect the overall discharge performance. Rather the reverse since the greater quantity of calcium chloride would lead to an increased conductivity of the electrolyte and be expected to increase the performance of the cell certainly in terms of on load plateau voltage.

The role of sulphur dioxide in corrosion protection.

Staniewicz (11) has shown that excess aluminium chloride exacerbated the corrosion problem of the calcium anode at open circuit. Since then all electrolytes that have been prepared by other workers in the field employed an excess of calcium chloride in order to minimise the amount of free Lewis acid available. Staniewicz (11) postulated that the attack of the aluminium chloride was via the calcium chloride SEI forming calcium tetrachloroaluminate (equation 10.1), thus reducing the protection this film offers to the calcium anode.
CaCl₂ + 2AlCl₃(SOCl₂)ₓ + xSOCl₂

-----→ Ca(SOCl₂)ᵐ⁺² + 2AlCl₄(SOCl₂)ⁿ⁻ ...(10.1)

The SEM investigation (chapter 9) and the weight loss experiments (chapter 4) have shown that the addition of sulphur dioxide reduces the corrosion of the anode by engendering a more tenacious film onto the calcium anode. The modified film has been analysed using ESCA (chapter 9) which shows the film to be comprised principally of calcium chloride. Only traces of sulphur containing compounds were found, so that the sulphur dioxide operation is not likely to be one of film doping. The greater protection must be attributed to a different crystal morphology and this has been shown (chapter 9) using the SEM technique. The more tenacious film explains the reduced corrosion rate seen with this electrolyte.

**Mechanism of operation of Calcium Thionyl Chloride cells**

From the analytical results obtained in chapter 5 and the physical data from chapter 9 the following mechanism is suggested for the operation of calcium tetrachloroaluminate thionyl chloride cells. It takes the form of a series of equilibria which are detailed below.

The three basic components that make up the electrolyte are thionyl chloride, aluminium chloride and calcium chloride (equation 10.2).

SOCl₂ + AlCl₃ + CaCl₂ ...(10.2)

In a saturated electrolyte the calcium chloride would be predominantly in its associated form and the components
of the above equation will produce, in neutral association, calcium tetrachloroaluminate. This can demonstrated to be true since 1.0M electrolytes can easily be prepared. Calcium chloride has a solubility in thionyl chloride (measured in chapter 5) of only $8 \times 10^{-5}$ M. If calcium tetrachloroaluminate did not form then the excess calcium chloride (above $8 \times 10^{-5}$ M) would be seen as a precipitate. This is not observed.

Thionyl Chloride has the relatively low dielectric constant of 9, dissociation of the calcium tetrachloroaluminate into its triple ions will be low. Since Ca(AlCl$_4$)$_2$ is a neutral species this will explain the low conductivity of the electrolyte. The conductivity will be engendered chiefly by the ionised species (CaAlCl$_4^{+}$ and Ca(AlCl$_4$)$_3^{-}$). Hence for a normal electrolyte the equilibrium sequence will be as shown in fig 10.1.

Sulphur dioxide has a much higher dielectric constant of 15, (when compared with thionyl chloride). This will allow further dissociation of the ionised species (CaAlCl$_4^{+}$ and Ca(AlCl$_4$)$_3^{-}$) into Ca$^{2+}$ and (AlCl$_4$)$^{-}$. Evidence for the formation of the above products comes from the increase in the intensity of the Ca$^{2+}$ band found in Raman studies of the sulphur dioxide system performed by Walker et al (53) and Loughborough University (54). These products explain why the conductivity is seen to increase on the addition of sulphur dioxide. Hence in a sulphur dioxide saturated electrolyte the equilibrium sequence will be as
Equilibria sequence for a normal Electrolyte.

Figure 10.1

\[
\begin{align*}
\text{SOCl}_2^+ & \quad \text{AlCl}_3^- + \quad \text{CaCl}_2^- \\
\text{Ca}^{2+} & \quad 2\text{Cl}^- \\
2\text{Ca(AlCl}_4^+)_2^- & \\
\text{CaAlCl}_4^+ & \quad \text{Ca(AlCl}_4^-)_3
\end{align*}
\]
shown in fig 10.2. The driving force of the further dissociation (into $\text{Ca}^{2+}$ and $(\text{AlCl}_4)^{-}$) will encourage more of the calcium tetrachloroaluminate to form the triple ions. This will in turn consume more of the aluminium chloride which may be a contributory factor to the reduced open circuit corrosion of the sulphur dioxide saturated system. The open circuit corrosion is however principally influenced by the crystal structure of the protecting SEI film, sulphur dioxide engenders a more tenacious tightly packed layer (see chapter 9 figs 9.1 - 9.10) which offers a greater degree of protection to the calcium anode.

**Cyclic Voltammetric and Impedance Data**

Both Impedance measurements and Cyclic voltammetry (at a rotating disc) show that the overall process is not controlled by mass transport in the bulk of the electrolyte. The impedance traces show no apparent Warburg diffusion process the spectra simply comprising a single time constant semicircle. Likewise there is no current limiting diffusion plateau in the voltammetry, the resistive nature of the SEI is suggested by the constant gradient of trace. These results demonstrate that the transport of charge carriers across the SEI is much slower than bulk diffusion in the electrolyte so that the former is the limiting process. Rotation speed independence confirms this.

The impedance measurements illustrate that three of the four electrolytes tested observe the same pattern (i.e. that the resistive semi-circle experiences a minimum diameter at some time after the initial contact between
Equilibria sequence for Sulphur Dioxide containing Electrolyte

Figure 10.2

\[ \text{Ca}^{2+} + 2\text{Cl}^- \]

\[ \text{SOCl}_2 + \text{AlCl}_3 + \text{CaCl}_2 \]

\[ 2\text{Ca}^{2+}(\text{AlCl}_4)_2 \]

\[ \text{CaAlCl}_4^+ + \text{Ca}^{2+}(\text{AlCl}_4)_3^- \]

\[ 2\text{Ca}^{2+} + 4(\text{AlCl}_4)^- \]
electrode and electrolyte). The other shows the resistive element increasing with time (i.e. the smallest resistance is on first contact). The explanation in chapter 8 is reinforced by the solubility data from chapter 5 and the longer term corrosion results presented in chapter 4. It was initially not thought necessary to measure the impedance traces after longer periods at open circuit since weight loss data was already available. However on reflection this would have been useful as it would have shown whether or not steady state corrosion behaviour was attained for each of the electrolytes.

**SEM studies**

These show the importance of the ability of the electrolyte to accommodate the reaction product i.e. calcium chloride. In a calcium chloride saturated electrolyte it has been demonstrated that above a particular load the anode passivates due to an increasing thickness of the precipitating anode film which effectively chokes off the passage of current, i.e. a dramatic increase in resistance to the movement of charge carriers through the reaction product film occurs.

**Conclusions**

The modified calcium calcium tetrachloroaluminate thionyl chloride cell has been seen to exhibit an increase in performance of around 300%, and a doubling of the shelf life over the initial base line system using a SAB cathode and a saturated calcium chloride, calcium
tetrachloroaluminate, thionyl chloride electrolyte.

The impedance measurements indicate that the open circuit corrosion rate can be estimated at much shorter times than is possible from weight loss data. Longer term impedance measurements should be undertaken to confirm this theory which would facilitate the screening of potential electrolytes to measure their relative corrosive nature.

In a recent paper Peled (55) gave the results for an improved performance calcium cell based upon a strontium tetrachloroaluminate electrolyte containing 20% sulphur dioxide, and utilising a fan to facilitate thermal management by cooling the cell. The best discharge results are ones where the power for the fan is taken externally rather than using the internal power of the cell.

It is shown in this work that the addition of sulphur dioxide to the electrolyte substantially reduces the open circuit corrosion rate (19). Peled stated that changing the electrolyte to strontium changes the morphology and the properties of the SEI layer. Adding sulphur dioxide to a calcium electrolyte has the same effect in that the SEI layer becomes more resistant to open circuit corrosion (chapter 4) and the cell can deliver a greater time on load before failure (chapter 6) SEM studies (chapter 9) have shown that sulphur dioxide engenders a more tenacious layer onto the calcium anode, whilst at the same time increasing the solubility of calcium chloride in the electrolyte. The increased solubility leads to a change from anode to cathode failure seen with referenced three electrode measurements,
and consequently an increased discharge performance.

The best discharge performance that we have obtained is with a balanced 1.0M calcium tetrachloroaluminate electrolyte with 10% sulphur dioxide, and utilising a cathode which contains 5% KC DJ600 by weight.

Peled's cell is pressurised with sulphur dioxide since saturation at atmospheric pressure is achieved at 10 - 12% by volume and since sulphur dioxide is itself a discharge product then pressurisation of the cell would appear to be a disadvantage with his system. His cell achieves a discharge capacity of 4.2 A Hr which is large but an anode area of 200 cm$^{-2}$ was used. This capacity corresponds to 21 mA hr cm$^{-2}$. He also uses a very thin (50 microns) separator paper. The separator used at Loughborough is much thicker (475 microns) and two of these papers were needed in order to stop shorting of the reference electrode. Hence the overall separator thickness is 950 microns. Using a thinner separator would lead to a better performance of the cell and if the reference electrode was removed then a paper similar to that of Peled's could be used.

The cell prepared at Loughborough gives 200 minutes to OV (figure 6.11) which corresponds to 33.33 mA hr cm$^{-2}$. At 50% depth of discharge (the same as Peled used) the plateau voltage is 2.34V. This represents a 37% increase in the discharge time over Peled's cell. There will be losses due to scale up of the cell but these could be minimised by careful cell design.
If the power for the fan is taken from the cell then the capacity to 2V drops to 2.69 A hr. That is 13.45 mA hr cm$^{-2}$ which gives an overall increase in performance of 45.5% when compared to his cell. The Loughborough cell has not been optimised in that it is still carbon limited. A higher proportion of DJ600 would lead to a further improved performance until anode failure again occurred. In addition the separator thickness could be greatly reduced which again would lead to an increase in the cells performance.

Summary

In recent months there have been a number of well documented cases involving lithium batteries and their related safety problems. The development of a commercially viable calcium oxyhalide system should provide a safe and reliable high performance battery for many years to come. The principle problem of open circuit corrosion is being addressed by a number of workers and preliminary results suggest that this drawback is not insurmountable.

At the present time the purity of commercially available calcium foils suitable for battery production is such that there are significant impurities mainly of group I and II metals. These impurities may well contribute to the excessive calcium anode open circuit corrosion. This situation will only be improved when calcium anoded cells are demonstrated to have a commercial future so that larger scale manufacture of purer calcium foils becomes economic.
References

1: E Peled, Advanced Calcium - Thionyl Chloride High-Power Battery Final Report Contract No. DAJA45 - 88 - C - 0012.


5: A Meitav and E Peled in Proc. of the 131st ISE Meeting, Venice, Italy (1980).


26: R.L. Higgins and J.S. Cloyd, Proc, 29th Power Sources
33: C.D.S. Tuck, Personal Communication.
38: Lovibond Palintest, The Tintometer Limited, Waterloo Road, Salisbury, Wilts.
54: W.P. Hagan et. al., Loughborough University, Unpublished Results.