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Method of Measuring Ohmic Resistance in Aluminium Reduction Cells

Mark Cooksey

ABSTRACT

The objective of this work was to develop a method of directly measuring the ohmic resistance in an industrial aluminium reduction cell. This requires that the voltage due to ohmic resistance be distinguished from the voltage due to the Nernst potential and polarisation. Electrochemical impedance spectroscopy can be used to directly measure ohmic resistance at the laboratory scale, but it is not suitable for an industrial aluminium reduction cell because an alternating current of the required magnitude and frequencies cannot be produced, and the system does not stay at steady state for the duration of the measurement.

A measurement technique was developed based on the principle of electrochemical impedance spectroscopy. A single bipolar pulse is generated by two capacitors. The current and voltage are measured and transformed to the frequency domain using Fast Fourier Analysis, from which the impedance at a range of frequencies is calculated. The ohmic resistance is the impedance where the imaginary impedance is zero (i.e. where there is only a real component).

Measurements were conducted on a physical electrical circuit designed to represent an industrial aluminium reduction cell. Inductance had a significant impact on the performance of the measurement technique, but the measurement parameters could be optimised such that the ohmic resistance of the circuit could be determined.

Measurements were conducted on a 500 A laboratory copper electrowinning cell with geometry similar to that of an industrial aluminium reduction cell. Inductance again had a significant impact on the performance of the measurement technique, but the measurement parameters could again be optimised such that the ohmic resistance of the cell could be determined.

This gives some confidence that the bipolar capacitor technique could be used to measure the ohmic resistance on an industrial aluminium reduction cell, and recommendations on how to conduct these measurements are provided.
ACKNOWLEDGEMENTS

I have benefited from the assistance and support of a large number of people during this PhD.

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I relied on Krishna Mohanaranagam to operate the copper electrowinning cell, and he was an enthusiastic and intelligent contributor.

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# LIST OF SYMBOLS

**Latin Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$c$</td>
<td>Velocity of wave</td>
<td>m.s$^{-1}$</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
<td>F</td>
</tr>
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<td>$d$</td>
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<td>$g$</td>
<td>Acceleration due to gravity</td>
<td>m.s$^{-2}$</td>
</tr>
<tr>
<td>$h$</td>
<td>Thickness of bubble layer under anode</td>
<td>m</td>
</tr>
<tr>
<td>$H$</td>
<td>Anode-cathode distance (ACD)</td>
<td>m</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density</td>
<td>A.m$^{-2}$</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>A</td>
</tr>
<tr>
<td>$k$</td>
<td>First order rate for coalescence</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$K_x$</td>
<td>Ratio of conductivity of mixture to conductivity of continuous phase</td>
<td>-</td>
</tr>
<tr>
<td>$l, L$</td>
<td>Length</td>
<td>m</td>
</tr>
<tr>
<td>$L$</td>
<td>Volume per unit area</td>
<td>m$^3$.m$^{-2}$</td>
</tr>
<tr>
<td>$L$</td>
<td>Inductance</td>
<td>H</td>
</tr>
<tr>
<td>$m, M$</td>
<td>Mass</td>
<td>kg</td>
</tr>
<tr>
<td>$n$</td>
<td>Number</td>
<td>-</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$Q$</td>
<td>Gas generation rate</td>
<td>m$^3$.s$^{-1}$</td>
</tr>
<tr>
<td>$q$</td>
<td>Gas generation rate per unit area</td>
<td>m$^3$.s$^{-1}$.m$^{-2}$</td>
</tr>
<tr>
<td>$q$</td>
<td>Electric charge</td>
<td>C</td>
</tr>
<tr>
<td>$R$</td>
<td>Radius</td>
<td>m</td>
</tr>
<tr>
<td>$R$</td>
<td>Real gas constant</td>
<td>J.mol$^{-1}$.K$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
<td>Ω</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t, T$</td>
<td>Time</td>
<td>s</td>
</tr>
</tbody>
</table>
**Greek Symbols**

- \(\alpha\) Anode inclination
- \(\varphi\) Phase angle
- \(\varepsilon\) Volume fraction of dispersed phase
- \(\eta\) Polarisation
- \(\kappa\) Electrical conductivity
- \(\lambda\) Wavelength
- \(\mu\) Magnetic Permeability
- \(\mu\) Viscosity
- \(\rho\) Density
- \(\rho\) Electrical resistivity
- \(\sigma\) Surface tension
- \(\theta\) Phase angle
- \(\nu\) Kinematic viscosity
- \(\omega\) Frequency
- \(\Theta\) Area fraction of dispersed phase on anode surface (gas coverage)
- \(\Omega\) Anode geometry

**Subscripts**

- \(a\) Anode
- \(b\) Bubble
- \(c\) Continuous phase
- \(ct\) Charge transfer
- \(d\) Dispersed phase
- \(dl\) Double layer
- \(e\) Electrolyte
- \(eg\) Electrolyte/Gas
g  Gas
l  Liquid
m  Metal
p  Pulse
s  Sampling
T  Total
x  Mixture of continuous and dispersed phase
Ω  Series (resistance)
SECTION A:

THEORY AND BACKGROUND
CHAPTER 1 – JUSTIFICATION

1.1 Hall-Héroult Process

Primary aluminium production is dominated by the Hall-Héroult electrolytic process, which was independently developed by Charles Hall (USA) and Paul Héroult (France) in 1886 (Thonstad et al. 2001: 1). The productivity and efficiency of the process has been improved significantly over the last century (Table 1.1), however the fundamentals of the process remain unchanged.

Table 1.1: History of performance of Hall-Héroult cells.

<table>
<thead>
<tr>
<th>Measure</th>
<th>1895*</th>
<th>1914**</th>
<th>1937**</th>
<th>1950**</th>
<th>1970***</th>
<th>1990***</th>
<th>2000***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line current (kA)</td>
<td>9</td>
<td>20</td>
<td>50</td>
<td>70</td>
<td>150</td>
<td>280</td>
<td>330</td>
</tr>
<tr>
<td>Productivity (manhours / ton)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>12</td>
<td>6</td>
<td>4.5</td>
</tr>
<tr>
<td>Current efficiency (%)</td>
<td>81</td>
<td>74</td>
<td>80</td>
<td>85</td>
<td>89</td>
<td>95</td>
<td>95.5</td>
</tr>
<tr>
<td>Energy requirement (DCkWh / kg)</td>
<td>31</td>
<td>26</td>
<td>21</td>
<td>20</td>
<td>15.5</td>
<td>13.2</td>
<td>13.1</td>
</tr>
</tbody>
</table>

*Haupin 1986  
**Welch 1986  
***Keniry 2001

There are two variations of the Hall-Héroult cell; Söderberg and prebake. In Söderberg cells, carbon paste is baked in situ to form a single anode. In prebake cells, the anodes are baked in a separate furnace prior to being placed into the reduction cell. The advantage of Söderberg cells is that a separate baking furnace is not required and there are fewer disturbances to the cell. The advantages of prebake cells are that the anode quality is higher, so carbon consumption is reduced, and there are lower cell emissions.

In 2008, world primary aluminium production was 86% prebake / 14% Söderberg (Marks and Bayliss 2010). In general, new smelters are constructed using prebake technology, and Söderberg technology at existing plants is gradually being replaced by prebake.

---

1 There is also one smelter operating continuous prebake anodes
technology (Syrdal 2002). Only prebake cells are addressed in this thesis, although the results could possibly apply to Söderberg cells.

Schematic diagrams of a cross-section and a top view of a prebake Hall-Héroult cell are shown in Figure 1.1 and Figure 1.2 respectively. Modern cells are typically 10-14 metres long and 3-4 metres wide, containing up to 50 anodes arranged in two parallel lines.

Figure 1.1: Schematic diagram of cross-section of prebake Hall-Héroult aluminium reduction cell (Burkin 1987: 48).

Figure 1.2: Schematic diagram of top view of prebake Hall-Héroult aluminium reduction cell.
The Hall-Héroult process is described as follows. Alumina (Al₂O₃) is fed to the cell once every few minutes or hours, depending on the cell technology. The alumina is dissolved in an electrolyte at ~960 °C that primarily consists of cryolite (Na₃AlF₆), with an excess of aluminium fluoride (AlF₃). Carbon anodes are positioned in the electrolyte and an electric current is passed down through the electrolyte to the carbon cathode below, at an anodic current density of 0.7-1.2 A.cm⁻² (Grjotheim and Welch 1988: 13). The aluminium ions are reduced to aluminium at the cathode and form a pool of molten aluminium. The aluminium metal is removed (‘tapped’) from the cell about once per day. The oxide ions are oxidised at the anode and combine with the carbon to form CO₂ and CO gas. There are two possible overall cell reactions, for which the electromotive force (emf) at 1000 °C at saturated alumina concentration for each reaction is (Thonstad et al. 2001: 159):

\[
2\text{Al}_2\text{O}_3(\text{diss}) + 3\text{C}(s) = 4\text{Al}(l) + 3\text{CO}_2(g) \quad E = -1.187 \text{ V} \quad (1.1)
\]

\[
\text{Al}_2\text{O}_3(\text{diss}) + 3\text{C}(s) = 2\text{Al}(l) + 3\text{CO}(g) \quad E = -1.065 \text{ V} \quad (1.2)
\]

The electromotive forces are relative similar, so kinetic considerations are important. There is universal agreement that reaction (1.1) dominates at industrial current densities (Thonstad et al. 2001: 158). The carbon anodes are consumed in these reactions and must be replaced every 2-3 weeks.

Aluminium electrolysis is a highly energy-intensive industry, representing approximately 13% of Australia’s electricity consumption from 2006 to 2009 (Australian Aluminium Council Ltd 2010). A modern aluminium reduction cell operates at 4.0-4.6 V (Grjotheim and Kvande 1993), and one breakdown of the contributions to this voltage is shown in Figure 1.3. These contributions can be summarised as shown in Table 1.2 and Equation (1.3).
Figure 1.3: Schematic representation of the voltage drop in an aluminium reduction cell (Haupin and Kvande 2000).

Table 1.2: Summary of contributions to cell voltage.

<table>
<thead>
<tr>
<th>Contribution to Cell Voltage</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromotive force</td>
<td>The potential difference created by the species at equilibrium (depends on temperature and concentrations of the various species)</td>
</tr>
<tr>
<td>Anodic and cathodic polarisation</td>
<td>The additional voltage beyond the electromotive force required for reactions to occur</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>The voltage drop across the region where electrolysis is occurring (the anode-cathode gap). This is due to the resistance of the electrolyte</td>
</tr>
<tr>
<td>Externals</td>
<td>The voltage drop across the other elements in the process, i.e. anodes, cathode, busbar etc.</td>
</tr>
</tbody>
</table>
\[ E_{cell} = E - \eta_a - \eta_c - IR_{elec} - IR_{ext} \]  \hspace{1cm} (1.3)

Where:
- \( E_{cell} \) = cell voltage
- \( E \) = electromotive force
- \( \eta_a \) = anodic polarisation
- \( \eta_c \) = cathodic polarisation
- \( I \) = electrical current
- \( R_{elec} \) = resistance of electrolyte
- \( R_{ext} \) = external resistance (anodes, cathode, busbar etc.)

There is incentive to address all the contributions described above. However, in many cases, the actions required to reduce the voltage drop may have a negative effect on other aspects of cell operation, e.g. the electrode polarisation can be reduced by reducing the current density, but this reduces metal production (assuming the anode area is kept constant).

According to Figure 1.3, the most significant contribution to the overall voltage is the electrolyte voltage drop, which is a function of the current and the resistance of the electrolyte. At a simplistic level, the resistance of the electrolyte is a function of the resistivity of the electrolyte, the anode-cathode distance (ACD) and the cross-sectional area of current flow.

The real situation in the anode-cathode gap (ACG) is more complex (Figure 1.4). CO\(_2\) gas bubbles are produced on the underside of the anode, so the ACG is not 100% electrolyte. This increases the resistance of the electrolyte. Note that according to Figure 1.3, bubbles are estimated to contribute 0.25 V to the overall voltage, in addition to the 1.33 V specifically due to the electrolyte. The voltage drop due to bubbles will be examined further in subsequent sections. From this point on in this thesis, the electrolyte voltage drop is taken to include the contribution of the gas bubbles.
The above discussion leads to three obvious methods of reducing the electrolyte voltage drop:

1. Move the anodes closer to the cathode, i.e. reduce the ACD. This approach is limited by the following:

   - Molten aluminium does not wet the carbon cathode\(^1\);

   \[
   F = J \times B \quad \text{(1.4)}
   \]

   \[\therefore\] Waves are produced in the aluminium metal pad.

---

\(^1\) Aluminium reacts with the carbon cathode to form aluminium carbide \((\text{Al}_4\text{C}_3)\), which is soluble in the cryolite electrolyte. Wetting of the cathode by aluminium is necessary to limit the dissolution of \(\text{Al}_4\text{C}_3\) by the electrolyte.
Chapter 1 – Justification

.: The anodes must be positioned a significant distance above the aluminium metal pad, to limit metal pad instability and the back reaction of aluminium to \( \text{Al}_2\text{O}_3 \), i.e. the ACD must be relatively large.

The aluminium industry is pursuing wettable cathodes (primarily \( \text{TiB}_2 \) composites) to address this issue, but this approach is not considered further here.

2. Reduce the resistivity of the electrolyte, by altering the chemical composition of the electrolyte:

There are limitations to the degree to which the composition of the electrolyte composition can be varied, due to the effect on other parameters. \( \text{LiF} \) has been used to reduce electrolyte resistivity, however this may introduce the need for a metal treatment step to remove the lithium.

3. Reduce the number and size of bubbles in the ACG.

The rate of bubble generation is approximately proportional to the current density, and is 0.17-0.30 cm\(^3\).s\(^{-1}\).cm\(^{-2}\) of anode area for a current density range of 0.7-1.2 A.cm\(^{-2}\) (assuming that \( \text{CO}_2 \) is the only gas produced in the electrochemical reaction). Therefore the amount of gas bubbles under the anode can only be reduced by increasing the rate of bubble removal. The contribution of gas bubbles to the cell voltage has only really begun to be recognised in the last 10-20 years. Therefore there is probably scope to improve bubble removal in aluminium reduction cells. This is the focus of this thesis.

1.2 Bubble Removal

In the last 20 years a significant proportion of industrial aluminium smelters have trialled and/or implemented ‘slotted anodes’ to enhance bubble removal. This involves incorporating one or more vertical slots in the anode to reduce the path length a bubble has to travel horizontally under the anode before it can freely travel upwards through the electrolyte. Schematic diagrams of two slotted anodes are shown in Figure 1.5. In general, the slot direction is defined in relation to the anode, i.e. a longitudinal slot is one that is
oriented in the longitudinal dimension of the anode, as in Figure 1.5a. The performance of slotted anodes has been mixed, with some smelters reporting benefits (Vanvoren et al. 2001; Bearne, Gadd, and Lix 2007), but others have removed the slots after a trial period (Rye, Myrvold, and Solberg 2007).

![Figure 1.5: Schematic diagrams of two simple slotted anodes.](image)

Bubble behaviour also affects electrolyte circulation, which has a significant effect on alumina dissolution and mixing. Control of alumina dissolution and mixing is important for conventional cells, but possibly critical for the implementation of advanced cell designs that are being researched by the aluminium industry. For example, it is likely that a cell using inert anodes will require tighter control of alumina concentration to prevent corrosion of the anode (Thonstad and Olsen 2001).

Returning to bubble resistance, a key issue is that it is difficult to directly measure the influence of the slots on bubble behaviour, because of the corrosive nature of cryolite at \(\sim 960 \, ^\circ C\). This makes it difficult to predict the effect of slot design on bubble removal. Because of these issues, the tendency has been to base slot design on other operational aspects, such as the direction that the anode is removed from the anode former. Only minor equipment modifications are required if the slot direction is parallel to the direction the anode is pushed off the former, while significant changes are required if the slot direction is perpendicular to the direction of anode movement. There is clearly a risk that non-optimal slot designs are being used in industrial anodes.
Because of the difficulties with in situ measurements described above, laboratory-scale electrolysis experiments and physical models have been used to study bubble behaviour. These approaches are compared in Table 1.3.

<table>
<thead>
<tr>
<th>Experimental Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature electrolysis on a small-scale cell</td>
<td>• Bubbles are generated as in an industrial cell</td>
<td>• Small scale means that bubble coalescence and fluid mechanics are different to industrial cell • Difficult to measure bubble behaviour</td>
</tr>
<tr>
<td>Room temperature electrolysis on a small-scale model</td>
<td>• Easier experimentation • Bubbles are electrochemically generated</td>
<td>• Small scale means that bubble coalescence and fluid mechanics are different to industrial cell • Bubble generation may be different to industrial cell</td>
</tr>
<tr>
<td>Physically generate bubbles on a full-scale model (physical model)</td>
<td>• Easier experimentation • Full-scale gives better simulation of bubble coalescence</td>
<td>• Bubble generation is different to industrial cell</td>
</tr>
</tbody>
</table>

Electrolytic methods of producing bubbles are preferred because they are more similar to an industrial cell. However it is difficult to conduct these experiments at full-scale because of the high currents involved. Physical models can be conducted at full-scale, however the bubble generation mechanism is different to an industrial cell. Therefore it is uncertain whether these modelling results can be directly applied to an industrial cell.

It is necessary to demonstrate that bubble behaviour in a physical model is representative of the situation in an industrial aluminium reduction cell. This will require measurements on industrial cells and possibly the construction of new types of models.

In summary there are the following needs for this research:

1. There is strong incentive to reduce the electrolyte voltage drop in aluminium reduction cells. The estimated voltage drop due to gas bubbles is approximately 1% of Australia’s electricity consumption;
2. Many aluminium smelters are modifying anode designs (e.g. installing slotted anodes) to increase the rate of bubble removal, without a sufficient understanding of the effects on bubble resistance and alumina dissolution and mixing;

3. Existing physical models may not be a sufficiently accurate representation of an aluminium reduction cell, particularly in respect to bubble generation and coalescence, for the purposes of measuring the number, size and velocity of bubbles;

4. Bubble behaviour in physical models of aluminium reduction cells has not been sufficiently quantified to allow the effect of different cell and anode designs to be evaluated with sufficient confidence, particularly in terms of the bubble resistance.

1.3 **Objective**

Based on the needs described above, the key objectives of this research are to:

1. Measure the bubble behaviour in an industrial aluminium reduction cell;

2. Demonstrate that a physical model can provide a sufficiently accurate representation of bubble behaviour in an industrial aluminium reduction cell, in terms of its effect on electrolyte resistance.
CHAPTER 2 – BUBBLE FORMATION

2.1 Introduction

The fundamentals of bubble formation are described briefly in this chapter. Particular attention is given to bubble formation on the underside of horizontal surfaces, which is applicable to aluminium reduction cells.

The fundamentals of electrolytic gas evolution are well covered in the literature (Sides 1986; Vogt 1983). Three distinct aspects of bubble formation can be considered:

1. Bubble nucleation;
2. Bubble growth;

In vertical electrolytic cells, detached bubbles rise rapidly in the electrolyte and leave the area of interest. However, in aluminium reduction cells, the relatively long residence time under the large horizontal allows bubbles to contact and coalesce. Because coalesced bubbles can conceivably become relatively large (in the order of the size of the anode), the release of such a bubble from the underside of the anode is a significant event. Therefore, two further aspects of bubble formation must be considered, in addition to the two listed above:

4. Bubble coalescence;
5. Bubble release.

These five aspects are discussed in the following sections.

2.2 Bubble Nucleation

In theory, the gaseous product of an electrolytic reaction exists as a dissolved species in the electrolyte. For example, one of the reactions occurring at the anode in an aluminium reduction cell is:
Chapter 2 – Bubble Formation

\[ 2\text{Al}_2\text{OF}_{8{\text{(diss)}}} + C_{(s)} = \text{CO}_2(\text{g}) + 4\text{AlF}_{4{\text{(diss)}}}^- + 4e^- \quad (2.1) \]

In this reaction, the CO\(_2\) product is initially dissolved in the electrolyte. However, in practice, the rate of CO\(_2\) production is such that it becomes supersaturated in the electrolyte and forms a gaseous phase, as per all gas-evolving electrodes (Vogt 1983: 446).

According to homogeneous nucleation theory, there is a critical radius of a bubble \(R_{\text{crit}}\) that is dependent on the liquid/gas interfacial tension \(\sigma_{eg}\) and the pressure of the gas and liquid (Vogt 1983: 447):

\[ R_{\text{crit}} = \frac{2\sigma_{eg}}{P_g - P_l} \quad (2.2) \]

Where: 
- \(P_g\) = sum of vapour pressure of pure solvent and partial pressure of dissolved gas
- \(P_l\) = pressure in liquid

Bubbles larger than the critical radius tend to grow and those smaller than the critical radius tend to decay.

The bottom surface of an industrial carbon anode has many imperfections, such as scratches and pits, which may contain entrapped gas. These can initiate further bubble formation. Equation (2.2) also applies to this situation; cavities with a radius larger than \(R_{\text{crit}}\) will grow via the supply of dissolved gas from the electrolyte.

2.3 Bubble Growth (via Diffusion)

Bubble growth is driven by several mechanisms. Firstly, there are driving forces from the pressure inside the bubble, the surface tension of the liquid and the density difference between the liquid and gas. These forces will cause bubble growth if they are greater than the forces resisting bubble growth (the inertial and viscous forces of the liquid acting on the bubble). The following equation has been derived for a spherical bubble (Scriven 1959):
Chapter 2 – Bubble Formation

\[ \frac{p_g - p_l - \frac{2\sigma}{R}}{\rho_l} = R R + \frac{3}{2} R^2 + 4 \frac{\mu}{\rho_l} \frac{R}{R} \]  \hspace{2cm} (2.3)

Where: \( \mu = \) viscosity of liquid

Convection causes dissolved gas to transport to the gas/liquid interface and add to the volume of the bubble.

Note that bubble size obeys the ideal gas law, i.e. increasing bubble size will be favoured by increasing temperature and decreasing pressure. This has been verified experimentally (Lans, Van Sandwijk, and Reuter 2004).

2.4 Bubble Growth (via Coalescence)

Coalescence is a second method of bubble growth. If bubbles collide, they will coalesce into larger bubbles. A variety of behaviour is observed depending on the gas-electrode-electrolyte system. Coalescence can occur between bubbles of a similar size into a larger bubble, or from a larger bubble ‘collecting’ surrounding smaller bubbles. It is not unusual for the final bubble size to be primarily a function of the degree of coalescence, rather than of the degree of bubble growth via diffusion.

2.5 Bubble Detachment

Bubbles detach when the surface adhesive forces are insufficient to hold the bubbles to the electrode surface. These forces are influenced by the contact angle of the bubble on the surface and the roughness of the surface. Bubbles have been observed to detach from the surface and then return to the surface, even on vertical electrodes (Sides 1986). It seems quite likely that this would occur under a horizontal electrode, because the buoyancy forces tend to force the bubble back to the electrode surface.
2.6 **Bubble Release**

Bubble release is the evacuation of a gas bubble from under a horizontal or near-horizontal electrode. This is an important aspect because a detached bubble will still contribute to resistance if it has not released from under the electrode. Investigations have been made for specific electrolytic systems (as will be described in Section B for aluminium electrolysis), however the fundamentals are not well understood.
3.1 Introduction

The effect of bubbles on the total voltage of an aluminium reduction cell is complex. There are several possible separate effects:

1. Bubbles have negligible conductivity compared to the electrolyte, hence bubbles reduce the conductivity of the electrolyte and cause increased ohmic resistance;
2. Bubbles on the surface of the electrode increase the local current density, which will increase the activation polarisation;
3. The bubble-driven flow takes bubbles away from the electrode surface, reducing supersaturation of the gas and reducing concentration polarisation;
4. In Hall-Héroult cells, the electrolyte is located above a layer of molten aluminium. Bubble release induces waves in the electrolyte/metal interface, which may affect the current path length and the overall resistance.

These are described briefly in the following sections, so as to provide some background to the reader before previous relevant studies are discussed in Section B.

3.2 Conductivity of Electrolyte

The ohmic voltage drop in the electrolyte $V_e$ is a function of the current $I$ and the resistance of the electrolyte $R_e$:

$$V_e = IR_e \quad (3.1)$$

At a simplistic level, $R_e$ is a function of the conductivity of the electrolyte $\kappa_e$, the anode-cathode distance $H$ and the area of the underside of the anode $A$:

$$R_e = \frac{H}{\kappa_e A} \quad (3.2)$$
However, the CO$_2$ gas bubbles that are electrochemically produced on the underside of the anode can be hypothesised to result in the situation shown in Figure 3.1.

![Simplistic model of bubble layer in the ACG under anode.](image)

**Figure 3.1:** Simplistic model of bubble layer in the ACG under anode.

The resistance in the ACG with bubbles present $R_{eg}$ is then the sum of the resistance of the electrolyte/gas layer and the resistance of the pure electrolyte in the lower part of the ACG:

$$R_{eg} = \frac{h}{\kappa_x A} + \frac{H-h}{\kappa_x A} \tag{3.3}$$

Where:
- $h$ = thickness of electrolyte/gas layer
- $\kappa_x$ = electrical conductivity of the electrolyte/gas dispersion

A second approach is to consider the electrolyte/gas mixture as separate phases of electrolyte and gas, and that the current can only flow through the electrolyte phase:

$$R_{eg} = \frac{h}{\kappa_x A(1-\Theta)} + \frac{H-h}{\kappa_x A} = \frac{1}{\kappa_x A} \left[ \frac{h}{1-\Theta} + (H-h) \right] \tag{3.4}$$

Where: $\Theta$ = the area fraction of anode covered by bubbles

---

1 The ‘gas coverage’
The effect of bubbles can also be expressed as a ratio of the resistance with bubbles present $R_{eg}$ to that with no bubbles present $R_e$:

$$\frac{R_{eg}}{R_e} = \frac{\frac{h}{\kappa_e A} + \frac{H-h}{\kappa_e A}}{\frac{H}{\kappa_e A}} = \left(\frac{\kappa_e}{\kappa_s} - 1\right) \frac{h}{H} + 1$$  \hspace{1cm} (3.5)

Or in terms of the incremental resistance $\Delta R$:

$$\Delta R = R_{eg} - R_e = \frac{h}{\kappa_e A} + \frac{H-h}{\kappa_e A} - \frac{H}{\kappa_e A} = \frac{h}{\kappa_e A} \left(\frac{\kappa_e}{\kappa_s} - 1\right)$$  \hspace{1cm} (3.6)

The above equations require an expression for $\kappa_e$. A fundamental relationship for the resistivity of a uniform dispersion of equal-sized spheres in a continuous phase is (Maxwell 1954):

$$\rho_s = \frac{2\rho_d + \rho_e + \epsilon(\rho_d - \rho_e)}{2\rho_d + \rho_e - 2\epsilon(\rho_d - \rho_e)} \rho_e$$  \hspace{1cm} (3.7)

Where: $\rho_s$ = resistivity of mixture  
$\rho_d$ = resistivity of dispersed phase  
$\rho_c$ = resistivity of continuous phase  
$\epsilon$ = volume fraction of dispersed phase

The electrical conductivity of gas bubbles is effectively zero, so for gas bubbles uniformly dispersed in a liquid phase, Equation (3.7) can be shown to simplify to:

$$K_s = \frac{1 - \epsilon}{1 + \frac{\epsilon}{2}}$$  \hspace{1cm} (3.8)
Where: \( K_x = \frac{K_s}{K_c} \) = ratio of electrical conductivity of mixture to electrical conductivity of continuous phase

This relationship only applies when the electrical disturbance from one bubble does not affect the disturbance from another bubble, i.e. at low volume fractions (e.g. \( \varepsilon < 0.1 \)). A number of other equations have been developed for higher volume fractions, such as:

\[
K_x = 1 - 1.5\varepsilon + 0.588\varepsilon^2 \quad \text{(Jeffrey 1973)}
\]

(3.9)

\[
K_x = 1 - 1.5\varepsilon + 0.5\varepsilon^2 \quad \text{(Prager 1963)}
\]

(3.10)

\[
K_x = \frac{1 - \varepsilon - 0.162\varepsilon^2 - 0.241\varepsilon^3}{1 + \frac{\varepsilon}{2}} \quad \text{(Chiew and Glandt 1983)}
\]

(3.11)

The above equations only apply for equal-sized spheres. For spheres of unequal size, the contribution of a pseudocontinuous\(^1\) range of progressively larger spheres can be progressively accumulated to show that (Bruggeman 1935):

\[
K_x = (1 - \varepsilon)^{\frac{3}{2}}
\]

(3.12)

It has been noted (Meredith and Tobias 1961) that Equation (3.12) predicted too low a conductivity at higher gas volume fractions, so the following relationship was derived:

\[
K_x = \frac{8(1 - \varepsilon)(2 - \varepsilon)}{(4 + \varepsilon)(4 - \varepsilon)}
\]

(3.13)

Equations (3.8) to (3.13) are shown in Figure 3.2. They are not individually labelled, as the purpose is to highlight the degree of agreement at different volume fractions of gas. It is also worth considering the maximum possible conductivity given a specific volume

---

\(^1\) ‘Pseudocontinuous’ means that each size fraction must be significantly larger than the previous size fraction, so this only applies where the range of size fractions is large.
fraction of gas. This would be the case where the gas is arranged in a homogeneous column parallel to the direction of the current. In this case:

\[ \kappa_s = \varepsilon \kappa_d + (1 - \varepsilon) \kappa_e \]  

(3.14)

Where: \( \kappa_d \) = electrical conductivity of dispersed phase

And since \( \kappa_d = 0 \) in the case of gas bubbles:

\[ K_s = \frac{\kappa_s}{\kappa_e} = (1 - \varepsilon) \]  

(3.15)

Note that this is the situation represented by Equation (3.4), i.e. the second approach of considering the electrolyte/gas mixture as separate phases of electrolyte and gas, and that the current can only flow through the electrolyte phase, is the minimum effect on resistance for a given volume fraction of gas.

Equation (3.15) is also shown in Figure 3.2. Thus, despite the uncertainties in the effect of gas bubbles on the conductivity of an electrolyte, the reduction in conductivity and corresponding increase in resistance will be at least the volume fraction of the gas (e.g. a gas volume fraction of 0.6 will produce at least a 60% reduction in conductivity and 60% increase in resistance).
Chapter 3 - Effect of Bubbles on Resistance

Figure 3.2: Comparison of equations to predict conductivity ratio $K_x$ as a function of gas volume fraction $\varepsilon$.

If Equation (3.15) is substituted into Equation (3.5), then:

$$\frac{R_{eg}}{R_e} = \left( \frac{1}{1-\varepsilon} - 1 \right) \frac{h}{H} + 1 = \left( \frac{\varepsilon}{1-\varepsilon} \right) \frac{h}{H} + 1 \quad (3.16)$$

In the case of a horizontal electrode, such as in a Hall-Héroult cell, bubbles also exist attached to the bottom of the electrode. A mathematical examination of a single bubble attached to an electrode found that the contribution to resistance was 10% less than a similar bubble in the bulk of the electrolyte (Sides and Tobias 1980). This is because the equipotential electrode terminates the disturbance in the potential, and so reduces the effect of the disturbance. It was also found that the effect of a bubble on potential becomes negligible more than three bubble diameters away from the electrode.

Overall, it has been concluded that the equations for bulk dispersions were reasonable for bubbles attached to an electrode (Sides 1986). This effectively means that the uncertainties in the equations for bulk dispersions are not significantly larger in the case of bubbles attached to an electrode.
3.3 Activation Polarisation

A voltage greater than the electromotive force is required to drive electrochemical reactions. Part of this overvoltage is the activation polarisation, which is required to overcome the activation energy of the reaction, and is related to the rate of electron transfer. The activation polarisation $\eta_{act}$ can be expressed in the form:

$$\eta_{act} = a + b \log\left( \frac{I}{A} \right)$$  \hspace{1cm} (3.17)

Where:  
$I = \text{current}$  
$A = \text{electrode surface area}$  
$a, b = \text{Tafel constants}$

The presence of bubbles on an electrode will effectively decrease the surface area of the electrode. From Equation (3.17) it can be seen that this will increase the activation polarisation.

3.4 Concentration Polarisation

At high current densities, the rate of an electrochemical reaction can be limited by the availability of ions at the electrode surface. Therefore a larger overvoltage is required to produce a given current. This is concentration polarisation. Bubbles can actually reduce concentration polarisation, because the evolution of bubbles agitates the electrolyte and assists the transport of fresh electrolyte to the electrode surface.

The gas flow in industrial cells is probably sufficient to mean that any small change in bubble behaviour will have a minimal impact on concentration polarisation. However, the elimination of bubble-driven flow (if it were possible) may result in higher concentration polarisation.

3.5 Current Path Length

The electrical conductivity of the electrolyte in an industrial cell is approximately 2 S.cm$^{-1}$, based on a number of studies (Thonstad et al. 2001: 115-120). The electrical
conductivity of molten aluminium is approximately $4 \times 10^4$ S.cm$^{-1}$ (Ben Abdellah, Gasser, and Grosdidier 2005); four orders of magnitude greater than the electrolyte. Therefore, the overall resistance of the electrolyte/metal system will be increased if the electrical current has to travel further through the electrolyte.

It is generally accepted that there is instability in the electrolyte/metal interface in industrial cells, due to a combination of magnetically-induced forces on the metal pad and the release of gas from under the anodes (Haupin and Frank 2002). The voltage signal of a cell is observed to contain components of varying frequencies (Bearne 1999), which supports the conclusion that there are multiple causes of variation in the voltage, one of which may be instability in the electrolyte/metal interface. Due to the huge difference in the electrical conductivity between the metal and the electrolyte, this variation may increase the voltage drop across the ACG.

### 3.6 Conclusions

Four possible contributions of bubbles to the total voltage of the cell were described in this chapter:

1. Increased ohmic losses due to the negligible conductivity of bubbles;
2. Increased activation polarisation due to bubbles on the surface of the electrode increasing the local current density;
3. Reduced concentration overvoltage due to bubble-driven flow reducing supersaturation of the gas at the electrode;
4. Increased ohmic losses due to bubble release causing waves in the electrolyte/metal interface and increasing the path length of the electrical current.

Studies of these contributions in industrial cells, laboratory cells and physical models are reviewed in Section B.
CHAPTER 4 – MEASUREMENT TECHNIQUES

4.1 Introduction

Many measurement techniques are used to study resistance in aluminium reduction cells. The purpose of this chapter is to describe the techniques reported in the literature so that the reader has some understanding of them before reaching Section B, where the relevant studies are reviewed. Techniques applicable to in-situ measurements in Hall-Héroult cells and measurements in laboratory-scale cells and physical models are covered.

4.2 Bubble Behaviour

4.2.1 Gas Flow

Several SINTEF studies have measured the amount of gas being evacuated from around an anode (Kobbeltvedt and Moxnes 1997; Moxnes, Aga, and Skaar 1998; Olsen, Rolseth, and Moxnes 1999). This technique involves placing a 15 cm wide funnel on the anode and measuring the time taken for the gas to displace a specific amount of silicone oil, to give the gas flow rate. Space restrictions can mean that the funnel can only be placed in certain areas at either end of the anode, and not at all in the inter-anode gap.

4.2.2 Gas Volume

Gas bubbles in a liquid will cause the liquid level to rise, which can be measured using a manometer. The increase in liquid level can be converted to a gas volume and a gas volume fraction, if the dimensions of the tank are known. This technique has been used for physical models of aluminium reduction cells (Solheim and Thonstad 1986; Zhang 1992). A weakness of the technique is that the contribution of all bubbles is measured, whilst often it is only bubbles in the ACG that are of interest.

4.2.3 Pressure Probe

A pressure probe has been used to measure the presence of bubbles in a Hall-Héroult cell (Walker 1995). It consists of a hollow tube that is placed into the electrolyte and
connected to a pressure transducer. Walker used an inconel tube (Ø13 mm OD, Ø8 mm OD) that could survive the corrosive environment for a sufficient length of time.

4.2.4 Anode Vibration

Bubble release will cause the anode to vibrate, and the acoustic signal on an anode rod has been measured to determine the vibration of an anode (Xue and Oye 1999).

4.3 Resistance

4.3.1 Contact Probe

Contact probes have been used to measure potential differences in Hall-Héroult cells, with the first reported use involving a tungsten probe protected by a boron nitride sleeve (Haupin 1971). In this method, the tip of the probe is incrementally moved upwards from the metal pad and the potential between the tip and the metal pad is measured. This allows the various components of the cell voltage to be investigated. The main limitations are the confounding of some voltage components and the short life of the probe (in the order of hours).

SINTEF has reported the use of a similar probe to detect the electrolyte/metal interface in Hall-Héroult cells (Rolseth, Solheim, and Thonstad 1988). Abrupt voltage changes are observed when the probe makes or breaks contact with the metal. The frequency of waves is measured by counting the number of abrupt voltage changes. The wave height is estimated by extrapolating the number of abrupt voltage changes to zero (representing either constant contact with electrolyte or constant contact with metal).

4.3.2 Anode Current

As already described, gas bubbles increase the resistance of the electrolyte. Since gas bubbles constantly generate, travel across the underside of the anode and release, this resistance will fluctuate. A cell is nominally supplied with constant current, but the fluctuating resistance of anodes arranged in a parallel circuit will produce a fluctuating current in each anode. This signal can be recorded and analysed to investigate the effect of bubbles.
The typical control strategy in industrial Hall-Héroult cells is to measure the current and voltage of the whole cell and analyse the calculated resistance to determine the cell condition. Individual anode currents are almost never measured as part of the control strategy due to the cost involved, with only a few exceptions. However, it is relatively common for individual anode currents to be measured on a small number of cells for a specific period of time, for trial purposes. The common technique involves measuring the voltage drop over a known length of the anode rod (Barber 1992). A variation is to measure the magnetic field produced by the current in the anode rod (Barclay, Hung, and Rieg 2001).

### 4.3.3 Applied Direct Current

A simple way of measuring the effect of bubbles on resistance in a physical model is to apply a constant voltage or current between two electrodes. For example, if a constant voltage is applied, then variation in the current will indicate the presence of bubbles. Examples are either a combination of a porous bronze plate as the anode and an aluminium sheet as the cathode, or embedded nickel electrodes into the anode surface and the bottom of the container to form an anode and cathode (Solheim and Thonstad 1986).

A weakness of this technique is that the applied current will produce polarisation at the electrodes if the voltage is above the decomposition voltage of the electrolyte. This polarisation can confound calculations of the resistance of the electrolyte.

### 4.3.4 Electrochemical Impedance Spectroscopy

This section is particularly relevant to the experiments conducted in this thesis. The discussions to this point have only involved direct current (DC). With alternating current (AC), the flow of charge periodically changes direction. The impedance $Z$ is the measure of opposition to alternating current (analogous to resistance for direct current). In this case, the current, voltage and impedance are all complex quantities, i.e. they contain a real and an imaginary component.
The magnitude of the impedance is the quotient of the magnitude of the voltage and current:

\[ |Z| = \frac{|V|}{|I|} \]  

(4.1)

The phase angle is the difference between the phase angles of the voltage and current:

\[ \phi = \phi_v - \phi_i \]  

(4.2)

And the real and imaginary components of the impedance can be calculated as follows:

Real: \[ Z' = |Z| \cos(\phi) \]  

(4.3)

Imaginary: \[ Z'' = |Z| \sin(\phi) \]  

(4.4)

At this point it is appropriate to introduce capacitance and inductance. A capacitor is a circuit element that resists changes in voltage. When a voltage is applied, current initially flows through the capacitor which acts as a short circuit, but over the time this causes voltage to build up on the capacitor, ultimately reaching the value of the applied voltage, but of opposite sign, thereby halting the flow of current. A common form of capacitor is two parallel plates.

An inductor is analogous to a capacitor, except that it resists a change in current. Initially a current passes through a conductor, but eventually this induces a current of equal but opposite sign, thereby halting the flow of current. A common form of inductor is a coil of wire.

Given that an AC signal is a rapidly oscillating current, a capacitor will act as a short circuit while an inductor will resist the change in current.

If a circuit contains capacitors and/or inductors, there will be a phase shift in the voltage compared to the current (i.e. \( \theta \neq 0 \)) and the impedance will have an imaginary component (i.e. \( Z'' \neq 0 \)). However, if the circuit contains only resistors, then there will be no phase
shift (i.e. \( \theta = 0 \)) and the impedance will have no imaginary component (i.e. \( Z' = 0 \)). In this case, the real impedance \( Z' \) will be equal to the resistance \( R \).

An electrochemical cell can be viewed as a total impedance \( Z_t \) to an AC signal, and can be represented by an equivalent circuit of resistors and capacitors. Electrochemical cells are commonly represented by the Randles equivalent circuit (Bard and Faulkner 2001: 376). An example is shown in Figure 4.1, where:

\[
R_{\Omega} = \text{series resistance, i.e. electrolyte + bubbles} \\
C_{dl} = \text{double-layer capacitance} \\
Z_f = \text{faradaic impedance, i.e. Nernst potential + polarisation. This only exists if there is a direct current sufficient to cause an electrochemical reaction.}
\]

The double-layer capacitance and faradaic impedance are in parallel because the AC signal passes through both components in parallel. The faradaic impedance can be considered in a number of ways, as shown in Figure 4.2. The components of the faradaic impedance change with frequency \( \omega \). The representation shown in Figure 4.2b consists of a charge-transfer resistance \( R_{ct} \) and a Warburg impedance \( Z_w \), the latter of which represents a resistance to mass transfer.

At high frequencies (i.e. as \( \omega \to \infty \)), the Warburg impedance \( Z_w \) in Figure 4.2 becomes negligible because diffusing reactants do not have to move very far. Therefore the equivalent circuit becomes as shown in Figure 4.3 (Bard and Faulkner 2001: 377-386).

![Randles equivalent circuit](image_url)

Figure 4.1: Randles equivalent circuit
Figure 4.2: Randles equivalent circuit, with faradaic impedance $Z_f$ represented as (a) a combination of an arbitrary resistance $R_s$ and capacitance $C_s$, and (b) a combination of a charge-transfer resistance $R_{ct}$ and Warburg impedance $Z_w$.

Figure 4.3: Randles equivalent circuit as $\omega \to \infty$, where Warburg impedance is negligible.

It can then be shown that, at high frequencies:

\[ Z' = R_\Omega + \frac{R_{ct}}{1 + \omega^2 C_{dl}^2 R_{ct}^2} \quad (4.5) \]

\[ Z'' = \frac{\omega C_{dl} R_{ct}^2}{1 + \omega^2 C_{dl}^2 R_{ct}^2} \quad (4.6) \]
Elimination of $\omega$ from Equations (4.5) and (4.6) gives:

$$
\left( Z' - R_\Omega - \frac{R_{ct}}{2} \right)^2 + Z'^2 = \left( \frac{R_{ct}}{2} \right)^2
$$

(4.7)

A Nyquist plot is a plot of $-Z'$ versus $Z'$, and for Equation (4.7) it will be a semi-circle, as shown in Figure 4.4. This provides a method of determining the series resistance $R_\Omega$ of an electrochemical cell: apply a range of high frequency AC signals to the cell and determine the value of $Z'$ when $Z'^2 = 0$. Modern electrical instruments can automatically apply a range of frequencies and determine the values of $Z'$ and $Z'^2$ at each frequency. This is Electrochemical Impedance Spectroscopy (EIS).

Note that there is not a universal convention for the definition of whether imaginary impedance due to capacitance is positive or negative. In this thesis, it is taken as negative, so the vertical axis of the Nyquist plot is $-Z'$, rather than $Z'$.

![Figure 4.4: Nyquist plot of equivalent circuit shown in Figure 4.3.](image)

**4.3.5 Luggin Capillary**

A Luggin capillary is designed to minimise the $IR$ drop in the measurement of voltage between a working electrode and reference electrode (Bard, Inzelt, and Scholz 2008). It is usually a bent, insulating glass tube, where one end contains the reference electrode and the tip of the other end is placed very close to the working electrode. The small distance
means that the $IR$ drop in the electrolyte is minimised, such that the voltage measured is primary a function of the Nernst potential and polarisation.

**4.4 Digital Signal Processing**

Digital signal processing is not a measurement technique in itself, but it can be used to characterise data acquired using the various techniques described above. Bubble release occurs at a higher frequency (~1 Hz) than the wave motion of the metal pad due to the magnetohydrodynamics (Chapter 1.1). Thus the high frequency component of the signal can be analysed using digital signal processing to determine its key features. For example, the DC component can be calculated as the mean of the overall anode signal. The intensity of the AC component can be calculated as the standard deviation of the remaining signal after the DC component had been subtracted. The relative contribution of the AC signal can be calculated as the AC/DC ratio.

The Fast Fourier Transform (FFT) technique can be used to decompose a signal into a series of signals of different frequencies. The relative magnitudes for the signals of different frequencies can indicate the dominant frequency of the original signal. Changes in these features can indicate changes in bubble behaviour.
SECTION B:

REVIEW OF RELEVANT STUDIES
5.1 Introduction

Studies of bubble behaviour in industrial aluminium reduction cells, including large pilot plant cells (e.g. 10 kA), are reviewed in this chapter. The studies are reviewed in order of progressively finer resolution, i.e. from interpretation of whole cell signals down to detailed measurements in the ACG.

5.2 Whole Cell Signals

A contact probe (as described in Chapter 4.3.1) was used to measure the potential between (a) the electrolyte just above the metal pad and the cathode busbar, and (b) the electrolyte near the anode and the anode busbar (Yang and Yang 1991). No numerical analysis was reported, but the pattern of fluctuations in the whole cell signal most closely matched that of (b). Since (b) was presumably due to bubbles, it was concluded that the high frequency fluctuation in the whole cell signal was due to bubbles.

Another study illustrates the influence of anode geometry on bubble behaviour and reduction cell performance (Bayer 1995). The standard AP30 anode arrangement consists of two anodes supported by a single anode rod. A trial was conducted to convert the two anodes into a single large anode by filling in the gap between the two anodes with additional carbon. This was expected to provide savings in anode handling. Unfortunately, a tripling of anode noise and an approximate 4% reduction in current efficiency occurred. More vigorous splashing of the electrolyte was observed around the larger anodes. Given that all other operational parameters appeared to be unchanged, the most logical conclusion is that the longer path length on the underside of the larger anode led to greater bubble coalescence and greater agitation of the electrolyte/metal interface following bubble release. A similar mechanism was observed in an internal Hydro report (in Moxnes, Aga, and Skaar 1998), where it was found that noise was significantly reduced by splitting the anodes in two.

The effect of bubbles on resistance has been highlighted by studies of the relationship between resistance and ACD. If bubbles had no effect, then the resistivity of the
electrolyte should be constant, irrespective of the ACD. In one study, temperature, voltage and current were continuously logged at various ACDs (Houston et al. 1988). It was found that resistivity increased with decreasing ACD, becoming asymptotic at an ACD of approximately 1 cm. Hence it was concluded that the bubble layer thickness was approximately 1 cm.

Similar behaviour was observed in 10 kA test cells being used for the development of TiB₂ cathodes (Dorward 1983). Assuming a gas-rich layer underneath the anode and the Bruggeman equation (Equation (3.12)), it was found that a bubble layer thickness of 1 cm gave good agreement with the observed increase in electrolyte resistivity with decreasing ACD. It was observed that voltage was linearly related to current, i.e. the resistance across the ACD was constant. Gas generation rate is proportional to current, so the bubble removal rate must have also increased if the overall resistance was unchanged. It was also speculated that anodic overvoltage may have been a confounding factor.

5.3 Gas Volume

Measurements of the amount of gas being evacuated from around an anode was first reported using the method described in Chapter 4.2.1 (Kobbeltvedt and Moxnes 1997). It was found that the gas flow varied between anodes, between the centre and side channel ends of one anode, and even between positions on one end of an anode. There was no consistent pattern to this variation. Another study reported that a longitudinal slot in the anode increased the gas flow exiting the side channel end of the anode by 83% (Moxnes, Aga, and Skaar 1998). A further study attempted to link the gas flow to the height of waves in the electrolyte/metal interface, but could only do so visually (Olsen, Rolseth, and Moxnes 1999).

Only a relatively small region was covered by each of the gas flow measurements described above, so these results do not necessarily represent an entire anode. In general, the gas flow rates did not correspond to that expected if the gas was evacuated purely on a geometric basis, i.e. along the shortest path length on the underside of the anode. The variation in gas flow rate due to both controlled and uncontrolled factors suggests that the distribution of bubbles on the underside of the anode is complex.
5.4 ACG Voltage

A pioneering study of the voltage drop across the ACG was conducted using the contact probe technique described in Chapter 4.3.1 (Haupin 1971). Measurements were reported for a 10 kA cell that had a large ACD (75 mm) and a relatively stable metal pad. The data showed that, in the bulk of the electrolyte, there was a linear relationship between the voltage drop and the distance from the metal pad (Figure 5.1). The voltage drop increased more rapidly very close to the anode surface, most likely due to bubbles. The voltage drop due to bubbles was determined by extrapolating the linear part of the curve to the point representing anode contact and calculating the difference between this extrapolated curve and the measured curve. Values of 0.09 to 0.35 V were obtained, which increased with increasing current density and decreasing alumina concentration.

The thickness of bubble layer was estimated at 2.1 cm, based on when the potential began to fluctuate significantly.

![Figure 5.1: Potential from metal pad to tip of probe in ACG (Haupin 1971).](image)
5.5 *Anodic Overvoltage*

Two studies (Richards 1998; Richards et al. 2003) used measurements of the anodic overvoltage to calculate the gas coverage of anodes. The following approach was used:

1. Calculated activation polarisation $\eta_a$ via:

$$\eta_a = a + b \log i_{an} - 0.005\text{wt}\%\text{Al}_2\text{O}_3$$

$$= 0.62 + 0.32 \log i_{an} - 0.005\text{wt}\%\text{Al}_2\text{O}_3$$

(5.1)

Where: Tafel constants $a$ and $b$ were obtained from laboratory studies (Richards and Welch 1965)

$i_{an} =$ nominal anodic current density

$\text{wt}\%\text{Al}_2\text{O}_3 > 2$

2. Calculated concentration polarisation $\eta_c$ via:

$$\eta_c = \frac{RT}{nF} \ln\left(1 - \frac{i_{an}}{i_L}\right)$$

(5.2)

Where: $R =$ real gas constant

$T =$ temperature

$n =$ number of electrons in reaction

$F =$ Faraday’s gas constant

$i_L =$ limiting current density $= 1.51 + 1.88\text{wt}\%\text{Al}_2\text{O}_3$

3. Measured the overvoltage $\eta_{obs}$ using a Luggin capillary (see Chapter 4.3.5)

4. Calculated the difference $\eta_{dev}$ via:

$$\eta_{dev} = \eta_{obs} - (\eta_a + \eta_c)$$

(i.e. Figure 5.2) (5.3)
5. Calculated the true current density $i_{at}$ by assuming that it was higher than $i_{an}$ solely due to the available anode area being reduced by bubbles, i.e:

\[
\eta_{dev} = \eta_{obs} - (\eta_a + \eta_c)
\]
\[
= (a + b \log i_{at}) - [(a + b \log i_{an}) + \eta_c]
\]
\[
= b(\log i_{at} - \log i_{an}) - \eta_c
\]
\[
\therefore \log i_{at} = \frac{\eta_{dev} + \eta_c}{b} + \log i_{an}
\]  

(5.4)

6. Calculated the gas coverage $\Theta$, via:

\[
\Theta = 1 - \frac{i_{an}}{i_{at}}
\]  

(5.5)

This approach seems reasonable, but the analyses are very sensitive to the Tafel constants. The same Tafel constants ($a = 0.62$, $b = 0.32$) are described in one study (Richards 1998) as being derived from a particular study (Richards and Welch 1965), while in the other study (Richards et al. 2003) they are stated to be a composite of results from numerous other researchers. Although the Tafel constants obtained in the study by Richards and Welch are reasonably consistent (e.g. within ±0.01 for a given alumina concentration), a wide variety of Tafel constants have been determined by different...
researchers (Thonstad et al. 2001: 161). It can be shown that a 1% change in \( a \) results in a change in gas coverage of more than 3% using the equations above, at typical alumina concentrations and current densities.

There are other minor discrepancies and possible sources of error in the above approach. The beginning of the derivation of Equation (5.4) states that \( \eta_{obs} = (a + b \log i_{at}) \), i.e. that there was zero concentration polarisation. It seems more likely that the measurement of \( \eta_{obs} \) would include \( \eta_c \), as shown in Figure 5.3.

\[
\begin{align*}
\therefore \eta_{obs} &= \eta_{at} + \eta_c \\
&= (a + b \log i_{at}) - 0.005\text{wt}\%\text{Al}_2\text{O}_3 + \eta_c \\
\therefore \log i_{at} &= \eta_{obs} + 0.005\text{wt}\%\text{Al}_2\text{O}_3 - \eta_c - a \\
&= \frac{\eta_{obs} + 0.005\text{wt}\%\text{Al}_2\text{O}_3 - \eta_c - a}{b} \quad (5.6)
\end{align*}
\]

![Figure 5.3: Alternative method to calculate gas coverage from overvoltage.](image)

However, the effect of this error is small as the value of \( \eta_c \) is small (<0.01 V) (Thonstad et al. 2001: 185). The gas coverage derived from using \( i_{at} \) as calculated from equation (5.6) is up to 2% lower than that using \( i_{at} \) as calculated from Equation (5.4). This is relatively insignificant given the ranges of gas coverages that were calculated (see Table 5.1).
The above analysis means that although the trends are probably valid, the absolute values of gas coverage must be treated with great caution.

The effects of current density, alumina concentration and anode design (presence of a longitudinal slot) on anodic overvoltage were measured. The current density was varied by raising or lowering the anode in the cell (Gudbrandsen et al. 2003). The calculations of true current density $i_{at}$ and gas coverage $\Theta$ have been based on Equation (5.6) and are summarised in Table 5.1 and Figure 5.4. It is apparent that $\Theta$ can be large and is highly sensitive to current density, alumina concentration and the presence of a slot.

As stated in Chapter 1.1, gas generation rate is approximately proportional to current density. The observation that gas coverage and hence the anodic overvoltage increase with increasing current density suggests that the increase in the rate of bubble removal (if any) is less than the increase in the gas generation rate.

Table 5.1: Summary of effect of current density and alumina concentration on anodic overvoltage and gas coverage (Richards 1998; Richards et al. 2003). ‘→’ indicates that the parameter was deliberately varied within the indicated range.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$T$ (°C)</th>
<th>$i_{an}$ (A.cm$^{-2}$)</th>
<th>wt% Al$_2$O$_3$</th>
<th>$\eta_{obs}$ (V)</th>
<th>$i_{at}$ (A.cm$^{-2}$)</th>
<th>$\Theta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 kA HSS* (Richards 1998)</td>
<td>970</td>
<td>0.8</td>
<td>5.0 $\rightarrow$ 1.2</td>
<td>0.59 - 0.95</td>
<td>0.9 - 10.4</td>
<td>10 - 92</td>
</tr>
<tr>
<td>965</td>
<td>0.6 $\rightarrow$ 0.9</td>
<td>4.2</td>
<td>0.50 - 0.72</td>
<td>0.5$^*$ - 2.2</td>
<td>0** - 59</td>
<td></td>
</tr>
<tr>
<td>180 kA prebake (Richards et al. 2003)</td>
<td>950</td>
<td>0.65 $\rightarrow$ 1.2</td>
<td>5.5</td>
<td>0.65 - 0.93</td>
<td>1.4 - 10.4</td>
<td>54 - 89</td>
</tr>
<tr>
<td>940</td>
<td>0.72</td>
<td>5.5 $\rightarrow$ 2.0</td>
<td>0.71 - 0.87</td>
<td>2.2 - 5.9</td>
<td>68 - 88</td>
<td></td>
</tr>
<tr>
<td>235 kA prebake (Richards et al. 2003)</td>
<td>975</td>
<td>0.65 $\rightarrow$ 1.0</td>
<td>2.3</td>
<td>0.66 - 0.93</td>
<td>1.3 - 9.2</td>
<td>50 - 89</td>
</tr>
<tr>
<td>975</td>
<td>0.65 $\rightarrow$ 1.0$^+$</td>
<td>2.5</td>
<td>0.58 - 0.82</td>
<td>0.8 - 4.2</td>
<td>17 - 76</td>
<td></td>
</tr>
</tbody>
</table>

*Horizontal Stud Soderberg

** $\eta_{obs}$ (0.50 V) < $\eta_{a}$ (0.54 V), which is a nonsensical result $\rightarrow$ assume $\Theta = 0$.

*Slotted anode: longitudinal slot, 1.5 cm wide by 13-16 cm deep
Figure 5.4: Effect of current density and alumina concentration on calculated gas coverage (results from Table 5.1).
If the large increase in anodic overvoltage with decreasing alumina concentration is solely due to an increase in gas coverage, then the bubble behaviour must have changed significantly as a function of surface tension or viscosity. It is also possible that the increase in anodic overvoltage is actually due to concentration polarisation, but this would mean that concentration polarisation is higher than as determined in a large number of laboratory studies (Thonstad et al. 2001: 185). It is interesting to note that the effect was much more substantial in the 150 kA HSS cell (0.36 V increase) than in the 180 kA prebake cell (0.16 V increase) for approximately the same decrease in alumina concentration. Perhaps electrolyte temperature has a significant effect (30 °C difference for the two cases).

The slotted anode was observed to have an overvoltage ~0.1 V less than a corresponding standard anode (at approximately the same alumina concentration), which translated to a large difference in gas coverage. Presumably, the slot facilitated gas removal. The absolute difference in gas coverage between a slotted and standard anode decreased at higher current densities. It was stated (Richards et al. 2003) that this indicates that a slot may not provide any benefit above 1 A.cm⁻². This is not a fair assessment, as the significance of a difference in gas coverage becomes greater at higher gas coverages. The true assessment of the benefit of a slot is its effect on overvoltage, which in this case was ~0.1 V, irrespective of current density.

In the same studies, the frequency and amplitude of the variation in the measured anodic overvoltage was analysed to determine the size of the larger released bubbles. The following approach was used (Richards 1998):

1. Calculated gas volumetric production rate based on current density, Faraday’s law and the ideal gas law (assumed gas was 100% CO₂);
2. Calculated area of anode covered by bubbles, using gas coverage as determined above;
3. Calculated bubble thickness, using the gas volume calculated in step (1) and the area of anode covered by bubbles in step (2);
4. Calculated area of anode covered by a single large bubble, assuming that the amplitude of the overvoltage (as a proportion of the total overvoltage) represented a
corresponding change in current density and available anode area (i.e. gas coverage) due to the release of a single large bubble;

5. Calculated the volume of a single large bubble, using the bubble thickness calculated in step (3) and the area covered by the bubble calculated in step (4);

6. Assumed that the frequency of release of large bubbles was that of the frequency of the variation in the overvoltage;

7. Calculated the relative contribution of large bubbles, using the volume of a single large bubble calculated in step (5), the frequency of release calculated in step (6), and the total gas production rate calculated in step (1).

Similar calculations were performed in a second study (Richards et al. 2003), but the calculations could not be reproduced. There is a flaw in step (3) in the method above. The volume of gas under the anode $V_g$ is not solely dependent on the volumetric production rate of gas $Q$: it is also dependent on the residence time of gas under the anode $t_g$ according to:

$$V_g = Qt_g \quad (5.7)$$

The second study (Richards et al. 2003) attempted to do this by calculating the gas volume produced between each release of large bubbles, i.e. taking $t_g$ as the time between the release of large bubbles. However, this is not necessarily $t_g$ for all gas under the anode. The two studies concluded that large bubbles were 100-400 cm$^3$, but the above errors mean that there is no basis to make this conclusion.

A Luggin capillary has also been used to determine the current density on the sides of an anode, by assuming the lower anodic overvoltage was due to a lower current exiting the sides of the anode (Gudbrandsen et al. 2003). The results indicated that the current density was 70-80% lower 9 cm above the base of the anode, compared to at the base of the anode.

5.6 Individual Anode Signals

There have been several studies that have used digital signal processing to analyse the signals from the current through an anode rod (Barber 1992; Walker 1995), the magnetic
field produced by the current through an anode rod (Barclay, Hung, and Rieg 2001) and the vibration of an anode rod (Xue and Oye 1999).

One study measured the voltage fluctuations in each anode in two industrial cells at 50 Hz for 20 second bursts every three hours (Barber 1992). One cell was a conventional Hall-Héroult cell and the other was a drained cathode cell, which is an experimental, modified Hall-Héroult cell that contains a cathode material that is wetted by molten aluminium (Thonstad et al. 2001: 333). Measurements were performed on anodes with 4° slope and on flat anodes (Figure 5.5).

The DC component, AC component, AC/DC ratio and dominant frequency were determined as described in Chapter 4.4. Results after two and 12 days are summarised in Table 5.2 (the anode rota was 13 days). The differences discussed below have been confirmed to be statistically significant.

In the conventional cell, it was found that the AC/DC ratio decreased from 2.2% to 1.3% over 10 days of operation. It was also found that the dominant frequency increased from 0.9 to 1.1 Hz. These results were attributed to the progressive rounding of the anode bottom profile as it was consumed, which would presumably promote the more frequent release of smaller gas bubbles.

Anodes in the drained cathode cell also exhibited a fluctuating current, although the patterns were significantly different. After two days, a significantly lower AC/DC ratio was observed on the sloped anode, compared to the anodes in the conventional cell. The dominant frequency was also higher than for anodes in the conventional cell, although Barber states that the signal was more evenly spread across all frequencies, and there was no single dominant frequency, for the sloped anode. It is plausible that the lower AC/DC ratio was due to the bubbles evacuating the ACG more quickly under the sloped anode, reducing the AC component.
The results in Table 5.2 could be further analysed, but will not be done so here. The specific relevance of Barber’s results to this thesis is that the drained cathode cell has no metal pad. Therefore it is unlikely that there was a significant wave in the electrolyte/metal interface. The fact that a voltage fluctuation of ~1 Hz frequency was observed in a drained cathode cell with no appreciable wave in the electrolyte/metal interface suggests that the similar signal in conventional cells is also due to a direct effect of bubbles, and not due to a wave in electrolyte/metal interface affecting the path of the electric current (as described in Chapter 3.5).

Another study performed similar measurements on two anodes in a conventional Hall-Héroult cell and obtained similar results to Barber (Walker 1995). Interestingly, Walker
concluded that the voltage fluctuation was primarily due to waves in the electrolyte/metal interface, rather than bubble release. However, his logic is not convincing. In particular, he assumed that similar signals on two different anodes could not be due to bubbles, since slight variations in anode geometry should significantly affect bubble behaviour. This is a subjective assessment and cannot be quantified. In comparing his results to Barber’s, Walker did not recognise the significant of the absence of the metal pad in the drained cathode cell.

Hall Effect sensors have been used to measure the magnetic field generated by the current flowing through anode rods at the Intalco smelter (Barclay, Hung, and Rieg 2001). It was preferred to have sensors on the front and back of the anode rod, to cancel any effect of the ambient magnetic field. However, a single sensor was also shown to perform adequately. It was found that different signals were produced in different anodes, which could sometimes be linked to cell condition.

The acoustic signal from the vibration of an anode rod in a 160 kA cell has been measured (Xue and Oye 1999). It was demonstrated that an anode with a spike\(^1\) produced a different signal to a ‘normal’ anode.

The last two methods discussed could be considered to be alternatives to measuring the fluctuation in the current flowing through an anode rod. The signal produced via any of the methods could be analysed using digital signal processing.

### 5.7 Pressure Fluctuations in Electrolyte

In parallel with the anode voltage measurements described above, the pressure fluctuations in the electrolyte have also been measured (Walker 1995), using the method described in Chapter 4.2.3. Measurements were made in the side channel adjacent to the two anodes where the anode voltage signals were measured. The pressure fluctuations were observed to be relatively well correlated to the voltage fluctuations, to the extent that they exhibited a similar dominant frequency.

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\(^1\) A protrusion of carbon downwards from the underside of an anode
5.8 Electrolyte/Metal Interface

There are two reported studies of the gas-induced wave height in the electrolyte/metal interface in 150 kA and 230 kA cells (Rolseth, Solheim, and Thonstad 1988; Olsen, Rolseth, and Moxnes 1999), using the method described in Chapter 4.3.1. In the former, waves up to 22 mm in height were measured in the 50 mm inter-anode gap. The maximum height of waves in the centre or side channel was only 13 mm. The frequency of waves was 0.2-0.6 Hz in the centre and side channels and 0.4-0.8 Hz in the inter-anode gap. The second study was more focused on the effect of a longitudinal slot and results were only reported for the side channel. The measured wave heights were comparable to the earlier study. The conclusion from this work was that higher waves and frequencies occurred in the inter-anode gap because the inter-anode gap was narrower than the centre or side channel. Thus the evacuating gas had more effect on the electrolyte/metal interface in this region. This logic appears sound.

5.9 Conclusions

It is well known that the cell voltage on an industrial cell fluctuates with a frequency in the order of 1 Hz, and the correlation between pressure fluctuation and anode voltage measurements is evidence that the fluctuation in cell voltage is due to gas bubbles. Anode geometry has been observed to significantly affect the cell voltage and current efficiency. In particular, very large anodes have been observed to produce a significant decrease in current efficiency. It is highly likely that this effect is due to changes in bubble behaviour.

Four possible contributions of bubbles to the total voltage of a cell were listed at the conclusion of Chapter 3:

1. Increased ohmic losses due to the negligible conductivity of bubbles;
2. Increased activation polarisation due to bubbles on the surface of the electrode increasing the local current density;
3. Reduced concentration overvoltage due to bubble-driven flow reducing supersaturation of the gas at the electrode;
4. Increased ohmic losses due to bubble evacuation causing waves in the electrolyte/metal interface and increasing the path length of the electrical current.
The work of Barber on drained cathode cells suggests contributions (1) and/or (2) are significant, because contribution (4) is very unlikely to be significant in a cell with no metal pad.

Haupin obtained values of 0.09 to 0.35 V for contribution (1), by extrapolating the relationship between potential drop and position within the ACD. The measurements were on a 10 kA cell with an ACD of 75 mm, which is quite different from a modern industrial cell, but the results can still be considered illustrative.

Measurements using a Luggin capillary have allowed contribution (2) to be examined, as the ohmic voltage drop in the electrolyte is minimised in these measurements. Richards et al. measured anodic overvoltages of 0.5 to 0.95 V on a range of cells, and found that it varied in a similar manner to the total anode voltage, which suggests that contribution (2) is significant.

Contribution (3) is assumed to be small, except as an anode effect is approached. The observation that anodic overvoltage increases significantly with decreasing alumina concentration suggests that concentration polarisation may be higher than is generally accepted, but it is more likely that there is an alternative explanation for this result.

Thus it can be hypothesised that bubbles:

- Have a significant effect on ohmic resistance in the electrolyte;
- Have a significant effect on activation polarisation;
- Have a relatively small effect on concentration polarisation;
- Have a relatively small effect on resistance via waves in the electrolyte/metal interface.

The anodic overvoltage (sum of activation and concentration polarisation) has been consistently measured to increase with increasing current density and decreasing alumina concentration, and the effects are very large. If the effects are to be explained solely in terms of available anode area, gas coverage on the underside of an anode must vary from zero to over 90%. In one study, a longitudinal slot has been measured to reduce anodic overvoltage by ~0.1 V.
Calculations of the apparent change in electrolyte resistivity suggest that the bubble layer is approximately 1 cm thick, however this is based on an idealised configuration of the bubble layer. Measurements of the potential between the metal pad and a point in the electrolyte suggest the bubble layer may be 2 cm thick.

There are several methods of measuring the fluctuation in current flowing through an anode: direct measurement of voltage, measurement of magnetic field around an anode rod, and measurement of vibrations in anode rod. The choice of technique would probably be based mostly on logistical considerations.
6.1 Introduction

Given the difficulties and expense of experiments in industrial cells, many researchers have chosen to undertake electrolysis experiments in the laboratory, where conditions can be better controlled. Studies of bubble behaviour in laboratory electrolytic cells are reviewed in this chapter. The focus is on aluminium reduction cells, but studies of other electrolytic processes with horizontal electrodes are also considered. There have been numerous laboratory-scale studies of electrolysis in vertical cells, which exhibit significantly different behaviour to horizontal cells. It is beyond the scope of this thesis to describe the literature in this area in detail.

In most laboratory studies the anodes used are of relatively small diameter (<100 mm), which is a significant simplification because coalescence of bubbles under a large horizontal anode is likely to have a significant effect on resistance. Coalescence also affects fluid flow, which can in turn affect bubble detachment and movement. Significant side currents may be induced because the walls of the crucible often serve as the cathode, which is different to the situation in industrial cells. Many studies use an alumina or boron nitride lining around the sides of the anode to ensure that only the bottom surface of the anode is exposed to the electrolyte.

6.2 Direct Observation

Several studies have allowed direct observation of the bubbles released at the surface during aluminium electrolysis. Very different bubble behaviour between a ferrite anode being tested as an inert anode and a graphite anode being used as a baseline has been observed (Peterson et al. 1990). The anode dimensions were ∅150 x 200 mm. With the graphite anode, bubbles releasing at the surface made a distinct ‘popping’ sound and produced a detectable vibration in the anode rod. With the ferrite anode, the bubbles were much smaller (almost a froth) and did not produce any sound or vibration. This is evidence that hydrodynamics (e.g. wetting of the anode by the electrolyte) has a significant effect on bubble behaviour.
Another study observed the formation of bubbles on the side of a $\varnothing 5$ mm anode (Cassayre, Utigard, and Bouvet 2002). The bubble nucleation frequency and the number of nucleation sites increased with increasing current density. Bubbles coalesced to be $\varnothing 2$-3 mm before detaching.

6.2.1 See-Through Cells

In 1975, experiments were reported on ‘see-through’ aluminium cells (Haupin and McGrew 1975). Initial tests were on quartz crucibles and graphite-lined quartz crucibles, however visual observation could only take place for only a few minutes before the quartz became opaque due to a reaction with a reduced phase produced in the melt. This phase was commonly referred to as a ‘metal fog’, but was actually believed to be a phase other than aluminium. Longer experiments could be completed with graphite crucibles containing a sapphire window. Bubbles were seen forming on the anode during electrolysis using all types of crucibles. It was observed that larger bubbles were favoured by decreasing oxide content. This was irrespective of whether the oxide was alumina or silica; the latter formed by dissolution of the quartz crucible. Increasing current density also produced larger bubbles, although it is believed that this observation was made on a vertical cell.

A similar quartz cell was used in another study, where the anode and cathode were in separate compartments (Qui et al. 1987). The metal fog eventually penetrated through fissures into the anode compartment and rose toward the bottom surface of the anode. The fog rose to within ~5 mm from the anode and began to fluctuate vigorously, and this situation was maintained for 30 minutes. The transparent layer between the fog and the anode was logically believed to be bubbles. To further illustrate the stability of the situation, the anode was raised by 15 mm and held in that position for several minutes, and then lowered by 15 mm back to the original position. In both cases, the metal fog ‘followed’ the anode and within a few minutes returned to the position of being ~5 mm from the anode. This is strong confirmation for the presence of a bubble layer under a horizontal anode.

Further studies on a quartz cell found that $\varnothing 0.4$-0.6 mm bubbles formed on the bottom surface of a $\varnothing 10$ mm anode (Xue and Oye 1995). These coalesced to a single bubble
4 mm thick and of diameter slightly greater than that of the anode, before detaching. An interesting observation was that the small initial bubbles exhibited a variety of behaviour. Some detached from the anode, but did not depart into the bath. Bubbles under the anode generally had an up and down motion and moved randomly to the anode edge. The movement of bubbles formed in the middle of the anode was impeded by other bubbles, so they coalesced.

Other researchers have also reported similar observation on a quartz cell, but found that experiments were not feasible at 0.7 A.cm\(^{-2}\) because the electrolyte rapidly became opaque (Cassayre, Utigard, and Bouvet 2002).

### 6.2.2 Radiography

There have been several reported observations of aluminium electrolysis using radiography (Utigard and Toguri 1986; Utigard and Toguri 1987a; Utigard and Toguri 1987b; Utigard, Toguri, and Ip 1988; Utigard et al. 1994; Cassayre et al. 2006; Cassayre, Utigard, and Bouvet 2002). The experimental cell typically consisted of a \(\varnothing3\text{-}18\) mm graphite anode inside a graphite crucible lined with a boron nitride or alumina cylinder.

In some cases, a single bubble was observed to cover the whole bottom surface of the anode; consequently the highest current density was on the lower sides of the anode (Utigard and Toguri 1986). It was consistently found that increasing the current density resulted in a smaller bubble diameter and an increased bubble release rate. This was also observed to produce a bubble layer of reduced thickness (Cassayre, Utigard, and Bouvet 2002). The effect of alumina content (over the range 0-10%) was less conclusive. In some cases it was observed to have no effect (Utigard and Toguri 1986; Cassayre, Utigard, and Bouvet 2002), however in one study a higher alumina content was observed to produce the formation of finer bubbles (Utigard et al. 1994).

A comparison was made between bubbles generated electrolytically and those generated when a variety of gases (Ar, CO\(_2\), CF\(_4\) and 15%H\(_2\)-85%N\(_2\)) were also supplied through a vertical hole in the centre of the anode (Utigard and Toguri 1986; Utigard, Toguri, and Ip 1988). Bubble growth in the latter configuration appeared to be similar to when bubbles were only generated electrolytically, including that supplying gas at a higher flowrate.
produced smaller bubbles that released more frequently. In one experiment, the cell polarity was reversed so that only physically generated bubbles were formed at the electrode of interest. The electrolyte wetted the electrode and a foam of very tiny bubbles formed at the gas discharge hole and immediately separated from the electrode.

Quite different bubble behaviour has been observed on inert anode materials compared to that on graphite, where the anode was Ø18 mm (Cassayre et al. 2006; Cassayre, Utigard, and Bouvet 2002). The inert anode materials were tin oxide, copper and 75/25 copper-nickel alloy. For graphite, the bubble layer thickness decreased from 5 mm to 4.2 mm as the current density was increased from 0.2 A.cm\(^{-2}\) to 1.6 A.cm\(^{-2}\).\(^1\) Conversely, for the three inert anode materials, the bubble layer thickness increased from almost zero at 0.2 A.cm\(^{-2}\) to ~2.2 mm at 1.0 A.cm\(^{-2}\), and then remained constant at higher current densities. The contact angle between the electrolyte and a graphite anode was measured to be 120-130\(^\circ\), while it was almost zero for inert anode materials.

The results described in the above two paragraphs indicate that the surface tension between the electrolyte and the electrode has a significant on bubble behaviour.

### 6.3 Gas Volume

A study used ten Ø2.5 mm probes arranged at different heights above the electrolyte around a Ø100 mm graphite anode to detect the increase in electrolyte depth due to bubbles (Aaberg et al. 1997). The height differential between each successive probe was 1.2 mm, which was stated to represent a bubble volume of 1 cm\(^3\), or 0.1 cm\(^3\).cm\(^{-2}\) of anode area. However, it can be shown that these figures are not consistent: with a Ø100 mm anode (i.e. bottom area 79 cm\(^2\)), 1 cm\(^3\) is equivalent to 0.013 cm\(^3\).cm\(^{-2}\) of anode area, an order of magnitude lower than 0.1 cm\(^3\).cm\(^{-2}\). It can be also shown that the gas production rate would be 8 cm\(^3\).s\(^{-1}\) (0.1 cm\(^3\).cm\(^{-2}\).s\(^{-1}\) of anode area) at 0.4 A.cm\(^{-2}\) (assuming 100% current efficiency and an operating temperature of 960 °C). This suggests that the probes were designed to detect a change in volume of 10 cm\(^3\), which is equivalent to 0.13 cm\(^3\).cm\(^{-2}\) of anode area; a more sensible figure and close to the value

\(^1\) It is believed that Figure 9 in (Cassayre, Utigard, and Bouvet 2002) has an incorrect vertical scale.
stated in the paper. This means that it would take ~1.2 s at 0.4 A.cm\(^{-2}\) for the bath height to rise 1.2 mm from one probe to the next probe.

It was found that the bubble volume at release was typically 0.4-0.6 cm\(^3\).cm\(^{-2}\) of anode area and only increased slightly with current density. The bubble volume remaining under the anode after release was close to zero. Bubble release frequency increased significantly with current density and actually increased more than would be expected (e.g. by a factor of 10 for a factor of four increase in current density), although there was large scatter in the results.

Another study based on similar apparatus also found that bubble release frequency increased with current density (Gao et al. 2005). There are some obvious errors in this paper, in that the bottom anode area was stated to be 67 cm\(^2\) for a $\varnothing$70 mm anode and 53 cm\(^2\) for a $\varnothing$60 mm anode, where they should be 38 cm\(^2\) and 28 cm\(^2\) respectively. It is assumed that the reported trends are unaffected by these errors.

In the first study, the bubble layer thickness under the anode just prior to bubble release was calculated by solving two simultaneous equations; one based on the calculated bubble volume and the other based on the measured resistance (Aaberg et al. 1997). There is insufficient detail in the paper to reproduce the calculations, and Equation (6.1)\(^1\) appears to be incorrect.

\[
d_h = \left(1 - \frac{1}{\varepsilon}\right) \left(\frac{R_{\text{total}} - R_{\text{external}}}{R_e} - H\right)
\]

(6.1)

Therefore, although it is stated in the paper that the bubble layer thickness was 0.5 cm, this cannot be verified.

### 6.4 Cell Voltage

There have been many studies of the voltage and resistance in laboratory-scale aluminium electrolysis cells. In an experiment at a relatively large scale: 75 h electrolysis at 200 A

\(^1\) Equation (8) in Aaberg et al. 1997
on a Ø152 mm anode, a significant change in the voltage signal was observed with time (Wang and Tabereaux 2000). Early in the experiment, the voltage exhibited a regular sawtooth pattern with amplitude 0.06 V and a dominant frequency of 0.9 Hz. Interestingly, a relatively abrupt change was observed in the voltage behaviour after 12 h of electrolysis: the frequency increased and the amplitude decreased. This could be attributed to rounding of the anode bottom surface and consequently the more frequent release of smaller bubbles. However, at the end of the experiment the alumina sleeve around the anode was found to be significantly degraded. Therefore it was concluded that the abrupt change in the voltage behaviour was due to failure of the alumina sleeve, which allowed side currents to form and significantly altered the current distribution.

In general, the frequency and amplitude of the voltage variation increased with current density, which was varied periodically. However, this effect changed during the course of the experiment: frequency became more dependent on current density and amplitude became less dependent on current density. No mechanism was suggested to explain this behaviour.

In a study previously discussed in Chapter 6.2 (Peterson et al. 1990), the voltage-time behaviour was very different between the graphite and ferrite anodes. For the graphite anode, the voltage exhibited a sawtooth pattern with a total variation of 0.1 V. The ferrite anode exhibited far less variation: 0.01 V. This suggests that the smaller bubbles observed on the ferrite anode resulted in a lower variation in the voltage. Note that this does not provide any information as to whether the average voltage induced by the bubbles was higher or lower for the ferrite anode.

It has been observed that the voltage varied more for a carbon anode compared to a SnO$_2$ inert anode, at the early stages of an experiment (Thonstad and Xiao 1992). However, the variation in the voltage for the carbon anode decreased significantly over the 2.5 h of the experiment, to the point where it is difficult to distinguish any difference between the carbon and SnO$_2$ anode in the figure presented.

A number of experiments conducted with a Ø30 mm anode and a TiB$_2$-carbon composite cathode, both with a 12° inclination, have been reported (Kasherman and Skylas-Kazacos
The bath resistivity was calculated for different ACDs (2-30 mm), using the assumption that all other voltage components remained constant. This assumed that the current density remained constant, which was acknowledged probably not to be the case due to side currents (7 mm of the sides of the anode were exposed to the bath) and changes in gas coverage affecting the effective anode surface area. Nevertheless, it was found that the bath resistivity increased significantly at low ACDs (Kasherman and Skyllas-Kazacos 1988), strongly suggesting the presence of a bubble layer.

It was found that the contribution of bubbles reduced with the addition of 5.5 wt% NaCl and increased with increasing excess AlF$_3$ content (Kasherman and Skyllas-Kazacos 1988). Experiments using a graphite anode and two carbon anodes showed that the bubble contribution was less for one particular carbon anode (Kasherman and Skyllas-Kazacos 1991b). These results show that the bubble contribution is sensitive to the electrolysis parameters.

A similar experimental setup has been used to evaluate the effect of ACD, anode immersion and anode inclination on voltage, mass transfer rate and current efficiency (Dorin and Frazer 1993). The anode was 24 mm and was sheathed with alumina for all but the bottom 1.5 mm. The molybdenum cathode was inclined at 5° and the anode was at the same angle for most experiments. Runs were typically 80 min at 5 A. The cell impedance was calculated by varying the current at 1 kHz and measuring the voltage at the same frequency. This allowed the ohmic voltage drop to be subtracted from the overall cell voltage to give a voltage that just represented the electrochemical reaction and the polarisation.

Close examination of the voltage revealed two distinct phenomena at the early stages of an experiment. Firstly, oscillations in the voltage of ~0.3 V with a dominant frequency of 0.3 Hz were attributed to the detachment of large bubbles. Secondly, smaller voltage oscillations between each pair of larger peaks had a spectrum of frequencies, with the largest voltage fluctuations at low frequencies (0-2 Hz). These were attributed to the growth and coalescence of bubbles.
Towards the end of a run, the distinct former pattern decayed into a smoother hump and was not very reproducible between experiments. It was concluded that the anode surface was changing in some way (e.g. becoming smoother) to favour the evolution of smaller bubbles.

A notable result was that the corrected voltage increased by 0.1 V with increasing ACD from 10 to 50 mm, even after allowing for the reduction in anode immersion with increasing ACD. No explanation could be found for this result. Further measurements to distinguish between the IR drop through external contacts and the IR drop through the electrolyte showed that the effective resistance of the electrolyte was higher at low ACDs; supporting evidence for the presence of bubbles.

With an ACD of 20 mm, the effect of anode inclination was tested at 0°, 5° and 48°, while the cathode inclination was maintained at 5°. The amplitude of the fluctuations in the cell voltage varied from 100-300 mV at 0° to 80 mV at 48°. This was attributed to the release of smaller bubbles as the anode inclination was increased.

In a study discussed previously in Chapter 6.2.1 (Xue and Oye 1995), the cell voltage behaviour was also studied by allowing one bubble to finally form and then depart the anode surface. At relatively low current densities (e.g. 0.25 A.cm⁻²), the voltage-time relationship exhibited two distinct stages between each pair of peaks in the voltage (corresponding to departure of the large bubble). In the first stage, the voltage increased linearly with time and this was attributed to the generation of small bubbles. In the second stage, the voltage increased more slowly with time and in a more random, fluctuating pattern. This was believed to be due to the growth and coalescence of the small bubbles. At higher current densities that are more typical of aluminium smelters (e.g. 0.75 A.cm⁻²), the first stage dominated at the expense of the second stage: the voltage-time signal exhibited a sawtooth pattern. The average increase in cell voltage due to a bubble was found to increase with current density, but only up to a current density of 0.50 A.cm⁻². Above this value it appeared that a higher frequency of bubble release compensated for the increase in current density.

The above study and another study by some of the same authors (Xue et al. 2005) investigated the effect of ultrasound. It was found that the application of ultrasound
decreased the cell voltage by ~0.1 V for a ∅10 mm anode at 0.25 A.cm⁻² (Xue and Oye 1995), and by 0.25-0.35 V for a ∅50 mm anode at 0.85 A.cm⁻² (Xue et al. 2005). The effect was mainly attributed to the ultrasound favouring the detachment of bubbles from the anode.

### 6.5 Anodic Overvoltage

 Richards made measurements of anodic overvoltage in laboratory cells in a similar manner to the industrial cell measurements discussed in Chapter 5.5 (Richards 1998). The laboratory measurements suffer from the same uncertainties as discussed in that chapter. The effect of current density and alumina concentration on measured overvoltage and calculated gas coverage was found to be similar to that in industrial cells (compare Figure 6.1 and Table 5.1). Again, it is difficult to believe that the increase in overvoltage with a decrease in alumina concentration could be purely due to a change in gas coverage.

### 6.6 Conclusions

There have been a large number of studies of aluminium electrolysis at a laboratory scale, all of which demonstrate that bubbles are present under horizontal anodes and have a significant effect on voltage/resistance.

Several experiments have demonstrated that the wettability of the electrolyte on the anode has a significant effect on bubble behaviour. Smaller bubbles that detach from the anode more rapidly are produced when the contact angle between the electrolyte and the anode was very small. This was achieved by either using an inert anode material such as ferrite or tin oxide, or by reversing the polarity of the cell. Even different types of carbon/graphite anodes produced different bubble behaviour. This conclusion is supported by both radiographic observation of bubbles and the observation that voltage fluctuations have a lower amplitude and higher frequency with inert anodes. The bubble layer thickness has also been observed to be less under an inert anode (0-2 mm) compared to a graphite anode (~5 mm).
Figure 6.1: Effect of current density and alumina concentration on measured overvoltage and calculated gas coverage (from Richards 1998)).

It has been consistently observed that smaller bubbles that release more frequently were favoured by increasing anode inclination. This applied for both inclination that was deliberately introduced and that was a result of rounding of the anode surface after some period of electrolysis.

Current density has been observed to have a significant effect on bubble behaviour. In general, increasing current density favours the formation of smaller bubbles that detach and release more frequently. In some cases this led to lower bubble layer thicknesses at higher current densities, which is somewhat surprising. Again, this is supported by both radiographic observation and voltage measurements. One study reported that increasing
current density produced larger bubbles, but it is believed that this observation was made on a vertical cell.

The effect of alumina concentration is more uncertain. Some studies have reported that bubble size decreases with increasing alumina content, but other studies have reported no effect. One study found that anodic overvoltage increased with decreasing alumina concentration. This was attributed to a change in gas coverage, but the magnitude of the effect is surprising.

Several studies reported that bubble release left the entire anode surface briefly clear of bubbles. Because of the relatively small anodes used, it is unknown whether this observation can be applied to industrial cells.
CHAPTER 7 – PHYSICAL MODELLING OF ELECTROLYSIS

7.1 Introduction

The previous chapter described how laboratory scale studies have been used to avoid the difficulties associated with experiments on industrial cells. The main weakness of the laboratory-scale approach is that the reduced scale of the experiments means that the electrolyte flow and bubble coalescence are not simulated accurately. An alternative approach is to use full-scale room temperature models of the process. This effectively exchanges one set of compromises for another: experiments can now be done at full-scale, but the conditions are now different from those in the industrial cell.

Room temperature physical modelling of electrolytic processes is reviewed in this chapter, with an emphasis on modelling of aluminium reduction cells. The focus is on studies relevant to resistance due to bubbles, so studies that are only focused on other aspects, such as current efficiency and heat transfer, are not considered, although they are of course important to industrial cell operations.

Laboratory-scale electrolysis studies that have used solid materials to simulate bubbles are discussed in this chapter, rather than Chapter 6.

7.2 Direct Observation

There has been an enormous amount of investigation of bubble behaviour in relation to vertical electrodes, but there have been only a few fundamental studies of bubble behaviour under horizontal electrodes. A study of bubble movement under a Plexiglas plate of 500 mm x 100 mm x 10 mm was undertaken where bubble movement was tracked directly by a camera and by the impact it had on the surrounding liquid (Perron, Kiss, and Poncsak 2005). Bubbles were observed to be stationary, creeping along the surface, or moving more rapidly along a film of liquid between the bubble and the surface. The creeping bubbles were elongated parallel to the direction of motion, whilst the moving bubbles were elongated perpendicular to the direction of motion. Increasing bubble volume and inclination favoured the moving bubble regime. Bubbles were
observed to affect the liquid to a depth of 4 cm, which was much larger than the thickness of the bubble.

A similar study was performed by injecting air into the centre of the top surface of an inclined box containing water (Che, Chen, and Taylor 1991). A transition in bubble shape was observed as the air flowrate was increased. Bubble coalescence was observed and found to be normally completed within 100 mm of the injection point. This value should be treated with caution, as bubble coalescence is likely to be quite different when bubbles are forming at multiple locations, as in an industrial cell. Increasing the anode inclination produced higher bubble velocities and lower bubble volumes.

The above discussion refers to the injection of a small amount of gas. More complete simulations of aluminium reduction cells are now considered.

The first reported study of bubble behaviour in a full-scale model of an aluminium reduction cell involved two 1350 mm x 400 mm x 660 mm anodes contained in a glass tank, also of 400 mm width (Fortin, Gerhardt, and Gesing 1984). Air was forced through a high density polyethylene plate via 15 chambers in each anode. A feature of this model was that the water was deliberately circulated through the model, rather than allowing the water motion to be solely bubble-induced.

When the anodes were horizontal, the bubbles gradually coalesced until they formed a single bubble covering the entire anode surface. This bubble then rapidly escaped, leaving a clean anode surface behind. The percentage of the anode surface area covered by bubbles was not influenced by gas injection rate; i.e. increasing gas flow rate only caused an increase in bubble release frequency.

An inclination of the anode of only a fraction of a degree resulted in very different bubble behaviour. Large bubbles were of the form shown in Figure 7.1, with a thick (up to 24 mm) leading edge and a thin (~5 mm) trailing edge. These large bubbles moved faster than smaller bubbles, hence they overtook and swallowed smaller bubbles as they moved along the anode surface. The effect of a number of parameters on bubble behaviour was investigated and is summarised in Table 7.1. ACD was found to have no effect on the measured parameters.
Chapter 7 – Physical Modelling of Electrolysis

Figure 7.1: Typical profile of large bubble travelling up anode inclination (Fortin, Gerhardt, and Gesing 1984).

Table 7.1: Summary of effects of gas injection rate, anode inclination and liquid velocity on bubble behaviour (Fortin, Gerhardt, and Gesing 1984). Parameters in brackets are defined in Figure 7.1.

<table>
<thead>
<tr>
<th>Change in controlled parameter</th>
<th>↑ Gas injection rate</th>
<th>↑ Anode inclination (α)</th>
<th>↑ Liquid velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect on measured parameter</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Longitudinal bubble dimension (l)</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Transverse bubble dimension</td>
<td>↑</td>
<td>↓/-</td>
<td>-</td>
</tr>
<tr>
<td>Bubble front thickness (h)</td>
<td>↑</td>
<td>-</td>
<td>↓</td>
</tr>
<tr>
<td>Bubble front width (w)</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
</tr>
<tr>
<td>% Gas coverage</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Bubble velocity</td>
<td>↑</td>
<td>-</td>
<td>↑</td>
</tr>
<tr>
<td>Bubble release frequency</td>
<td>-</td>
<td>↑↑</td>
<td>↑</td>
</tr>
</tbody>
</table>

More recent modelling was performed on a half anode with a porous brass plate (Cassayre et al. 2006). Similar trends to that of Fortin, Gerhardt and Gesing were observed. Even a narrow slot (5 mm) had a significant effect on the flow of bubbles.

In another study, an 800 mm x 208 mm anode was contained in a Plexiglas container of the same width (Solheim and Thonstad 1986). The model was inclined slightly so that there was one-dimensional liquid flow towards the side channel. Three anode bases were used:

1. Plexiglas plate with one Ø0.5 mm hole per cm² of anode surface;
2. Porous bronze plate;
3. Cotton cloth between two perforated aluminium plates.
Similar bubble behaviour was observed for the latter two materials, whilst the initial bubbles were slightly larger on the Plexiglas plate. A significant difference was found after the addition of 1-propanol to reduce the surface tension of the water. This slightly reduced the bubble size on the Plexiglas plate, but caused a very significant change in bubble behaviour on the other two materials. The initial bubble size was drastically reduced and coalescence did not occur to the same degree.

An inclined manometer was used to measure the liquid level and calculate the accumulated gas volume, as described in Chapter 4.2.2. It was found that reduced bubble size (via the addition of 1-propanol) resulted in an increase in the accumulated gas volume by up to four times. This result applied for a range of ACDs, gas injection flowrates, anode inclinations and liquid viscosities (via the addition of glycerol).

This result is not surprising. For a given injection flowrate, the gas volume injected into the system is independent of bubble size. Smaller bubbles will rise more slowly than large bubbles, due to the drag force increasing more than the buoyancy force (Clift, Grace, and Weber 1978: 33). Therefore smaller bubbles will have a longer residence time and hence a higher accumulated gas volume. However, this does not necessarily mean that the accumulated gas volume is higher in the ACG. The extra gas may all be in the side channel, where it would have no impact on electrical resistance.

As a comparison to the experimental results, an expression was derived for the accumulated gas volume per unit anode area $L_b$ by balancing the forces acting on a bubble, making a number of other assumptions (such as $f(d, \varepsilon, \Theta) = 1$) and partly using an empirical expression derived from the experimental data:

$$L_b = \left( \frac{qX^3 \nu}{(g \cdot \sin \alpha)^2} \right)^{0.2} \left( \frac{H}{0.04} \right)^{-0.1} f(d, \varepsilon, \Theta)$$  \hspace{1cm} (7.1)

Where:

- $q$ = gas generation rate
- $X$ = distance from centre to edge of anode
- $\nu$ = kinematic viscosity
This equation applied for ACDs >2 cm and showed very good agreement with the experimental data, but this is not surprising since the equation was partly based on the experimental data.

A series of studies compared the bubbles generated in an air-water model with those in an electrolytic room temperature model with a 2M NaOH electrolyte (Qian 1999; Qian, Chen, and Matheou 1997; Qian, Chen, and Chen 1998; Chen, Qian, and Zhao 2001). The anodes were 100 mm x 40 mm, to limit the electrical current to a practical level for experimentation. In the air-water model, there were mostly large bubbles with areas totally clear of bubbles. In the electrolytic model, there were few large bubbles and most of the anode was covered by a layer of tiny bubbles (<∅0.5 mm). Bubbles coalesced as they moved along the underside of the anode. Gas coverages were calculated on the basis of bubbles >∅0.8 mm (the smallest that could be accurately resolved on the video monitor).

The effect of bubble behaviour on current efficiency has been comprehensively studied (Zhang 1992). A 1:2.5 scale model of an anode, side channel and ledge¹ was constructed, and the gas bubbles were generated by forcing air through a porous bronze plate through five independent chambers. Water (with additions of 1-propanol for some experiments) was used as the electrolyte and C₆H₅Cl was used to represent the metal layer. The gas injection rate was varied from ~0.3 to ~1.0 A.cm⁻², in terms of the current density it represented.

¹ Ledge: a term used in the aluminium industry to describe the frozen electrolyte that forms on the internal surface of the sidewalls.
Gas was observed to be present to a depth of 2-3 mm under the anode at the centre of the anode, and 5-8 mm at the edge of the anode. This was affected by the current density and anode inclination.

Bubble shape was observed to depend on bubble velocity. Below ~14 cm.s$^{-1}$, the bubbles were elliptically shaped (when viewed from below) and 2-3 mm thick. At higher speeds, the bubble front was thicker (up to 8 mm) and had a thin trailing edge. Very few bubbles were observed in any other region other than that immediately adjacent to the bottom surface of the anode.

A manometer was used to measure the liquid level and calculate the gas volume fraction, as described in Chapter 4.2.2. Note that the measurement of liquid level incorporates the presence of all bubbles in the liquid, not just those under the anode. The gas volume fraction increased with increasing gas injection rate, increasing electrolyte viscosity, decreasing surface tension and decreasing anode inclination. The effect of viscosity may have been due to bubbles rising more slowly in the side channel and hence having a longer residence time, rather than there being a greater bubble volume under the anode. Interestingly there was a step change at about 2$^\circ$ anode inclination, indicating that a change in bubbling mechanism had occurred.

Another study utilised a simple physical model of half an anode (Li et al. 2004). Air was introduced through 150 holes drilled in the base, which is an even poorer representation of an industrial cell compared to having a porous bronze or polymer base. Increasing anode inclination and ACD were both found to decrease the residence time of bubbles under the anode.

7.3 Resistance

There have been two sets of work that examined the effect of bubbles on resistance in water models of aluminium reduction cells in some detail. Observations of bubble behaviour in the first study were discussed in Chapter 7.2 (Solheim and Thonstad 1986). The effect of bubbles on resistance was determined by measuring the magnitude of a DC current passing through the electrolyte while keeping the voltage constant at 15 V, as per
the method described in Chapter 4.3.3. As this voltage is above the decomposition voltage of water (1.23 V), the current was kept low to minimise polarisation at the anodes.

Equation (3.5) was modified by using the fact that the increase in resistance due to gas $\Delta R = R_{eg} - R_e$ and the accumulated gas volume per unit area $L_b = \varepsilon H$:

$$
\frac{\Delta R}{R_e} = \frac{R_{eg} - R_e}{R_e} = \left(\frac{\kappa_e}{\kappa_{eg}} - 1\right) \frac{h}{H} + 1 = \left(\frac{\kappa_e}{\kappa_{eg}} - 1\right) \frac{L_b}{\varepsilon H}
$$

$$
\therefore \frac{\Delta R H}{R_e L_b} = \left(\frac{\kappa_e}{\kappa_{eg}} - 1\right) \frac{1}{\varepsilon}
$$

(7.2)

Combining Equation (7.2) with Equation (3.12) (the Bruggeman equation) gives:

$$
\frac{\Delta R H}{R_e L_b} = \left(1 - \varepsilon^{-1.5} - 1\right) \frac{1}{\varepsilon}
$$

(7.3)

The densest possible packing of equally sized spheres gives $\varepsilon = 0.74$, which gives $\frac{\Delta R H}{R_e L_b} = 8.8$ according to Equation (7.3). The authors state that since the resistance and accumulated bubble volume measurements showed that $\frac{\Delta R H}{R_e L_b}$ could be greater than 8.8, this meant that the Bruggeman equation did not apply to this situation. This is unsurprising as the Bruggeman equation does not apply to equal sized spheres (Chapter 3.2).

It was found that the increase in resistance showed greater variability than the accumulated gas volume, and it was concluded that this meant that the conductivity of the bubble layer did not remain constant. An alternative explanation could be that the accumulated gas volume under the anode could have varied more than the overall accumulated gas volume, and hence could have correlated better with the increase in resistance.

Dimensional analysis was used to derive an expression:
\[ \frac{\Delta R}{R_e} \frac{H}{L_b} = \frac{qXk}{Hg \sin \alpha} \left( \frac{H}{d_0} \right)^{0.8} \] 

(7.4)

Where:

- \( d_0 \) = initial diameter of bubbles
- \( k \) = first order rate for coalescence

Other terms defined as per Equation (7.1)

By graphing the left hand side of Equation (7.4) against the right hand side, it was stated that \( \frac{\Delta R}{R_e} \frac{H}{L_b} \) was higher for smaller bubbles, i.e. that the increase in resistance was greater for smaller bubbles. However, the initial bubble size \( d_0 \) was assumed to be unity for the purposes of the calculation (because it could not be determined accurately), despite the observation that the bubbles sizes were clearly different. If plausible values of \( d_0 \) are substituted into Equation (7.4), then there may not be any relationship between resistance and bubble size.

The second set of work studying the effect of bubbles on resistance in physical models was also discussed in Chapter 7.2 (Qian 1999; Qian, Chen, and Matheou 1997; Qian, Chen, and Chen 1998; Chen, Qian, and Zhao 2001). The effect on resistance was reported in terms of bubble resistivity ratio \( \frac{\rho_{eg}}{\rho_e} \).

EIS, as described in Chapter 4.3.4, was used to determine the bubble resistivity ratio. In the air-water model, increasing bubble resistivity ratio was favoured by increasing current density, decreasing ACD, decreasing anode inclination and decreasing surface tension. Increasing the viscosity of the water also produced a small increase in the bubble resistivity ratio. Varying the conductivity of the water had minimal effect on the bubble resistivity ratio.

Anodes constructed from graphite and from part of a spent industrial carbon anode were compared in the electrolytic model. At 2° anode inclination, the carbon anode produced a higher bubble resistivity ratio. However there was no difference at 8° anode inclination. It
was concluded that the rounded geometry of the carbon anode favoured bubble release and hence lower bubble resistivity ratio, and that this effect was lessened as the anode inclination increased. This appears to be a reasonable conclusion.

Measurements of bubble resistivity ratio and gas coverage at a range of current densities and anode inclinations on both models showed that bubble resistivity ratio increased linearly with gas coverage, for a given ACD:

\[
\frac{\rho_{es}}{\rho_e} = a + b\Theta
\]  

(7.5)

Where: \( \Theta \) = area fraction of bubbles on underside of anode  
\( a, b \) = constants

For a given gas coverage, the bubble resistivity ratio was consistently higher on the electrolytic model compared to the air-water model. This was attributed to the measured gas coverage on the electrolytic model being an underestimate of the true gas coverage, because a large proportion of bubbles in the electrolytic model were smaller than the minimum \( \Phi 0.8 \) mm bubbles that could be counted.

Many correlations of bubble resistivity ratio with ACD are of the form:

\[
\frac{\rho_{es}}{\rho_e} = \frac{M}{H} + 1
\]  

(7.6)

Where: \( M \) = an expression  
\( H = \) ACD

If Equation (7.6) is valid, it can be shown that:

\[
\frac{\rho_{es}}{\rho_e} = \frac{a_1 + H - 1}{H} + \frac{b_1}{H} \Theta
\]  

(7.7)
Using the data for ACD = 1, Qian found that using Equation (7.7) to predict the bubble resistivity ratio for ACDs of 2 to 6 cm gave very good agreement to the measured bubble resistivity ratio at these ACDs. This suggests that Equation (7.6) is a good expression of the effect of ACD on bubble resistivity ratio.

Several studies have used solid materials to simulate bubbles under horizontal anodes. One set of experiments involved placing a hexagonal array of machined spheres on the bottom of an electrode (Sides and Tobias 1982). It was found that the overall conductivity was slightly greater than predicted by the equations for equal spheres in bulk dispersions, for volume fractions up to 0.4.

In another study, ceramic beads and glass disks were introduced on the underside of the upper electrode in the electrosmelting of lead from a 28%NaCl-72%PbCl₂ solution (Hyde and Welch 1997). The upper electrode was made the cathode to avoid interference from chlorine bubble formation. It was found that the cell resistance increased linearly with sphere volume for a range of sphere sizes from ∅5.3-12.5 mm (for a monolayer of spheres). The disks produced some scatter in the results, but the linear relationship between ceramic/glass volume and resistance still held.

Similar experiments involving glass spheres of 2, 3, 6 and 12 mm diameter during the electrolysis of KCl at room temperature have been performed (Janssen 2000). Similarly, the resistance was linearly related to the volume of the glass spheres. It was also found that the increase in resistance was within 8% of that predicted according to the Bruggeman equation (Equation (3.12)).

7.4 Electrolyte/Metal Interface

It was stated in Chapter 3.5 that the release of bubbles causes fluctuations in the electrolyte/metal interface. This phenomenon has been examined using physical models. The first reported study was used water and silicone oil to simulate the electrolyte and liquid metal, respectively, in a 2D model of one anode (Dernedde and Cambridge 1975).
Electrolyte/metal interface waves up to 16 mm in amplitude were observed. Ledge was simulated in the model and was found to reduce the amplitude of electrolyte/metal interface waves. This was believed to be because the ledge restricted the silicone oil to an area smaller than the anode shadow, which reduced the effect that the gas release up the sides of the anode could have on the electrolyte/metal interface.

A more comprehensive study used a full-scale model of 40% of a 90 kA cell (eight anodes) (Chesonis and LaCamera 1990). The amplitude of the electrolyte/metal interface waves was much larger in the inter-anode gap compared to under the anode. This amplitude increased with decreasing ACD, increasing current density and increasing bath depth, and was larger for anodes with square corners compared to those with rounded corners. This last effect was investigated more closely on a two-anode model of the same cell. Inter-anode gap and the profile of the anode corner had an interactive effect on the amplitude of electrolyte/metal interface waves, illustrating the complexity of the mechanisms at work.

7.5 Conclusions

The bubble layer under the anode has been observed to be up to 24 mm thick. Significant variations in bubble size and shape have been observed from model to model, and even on the same model if certain parameters were varied. In particular, surface tension and the anode surface material were found to have a significant effect. It would be unwise to predict bubble size and shape in an industrial cell on the basis of observations on physical models.

It has been observed that moving bubbles can either be attached to the surface or have a thin film of liquid between the bubble and the surface, depending on bubble velocity. This is an important observation, because the difference between these two mechanisms may affect the true current density and hence the anodic overvoltage.

In general, increasing anode inclination has been observed to favour higher bubble velocities and lower bubble volumes. There was one exception where it was found to have no effect on bubble velocity. The resistance across the ACG was observed to be
lower at higher anode inclinations, which corresponds to the presence of less bubbles under the anode.

Experiments where bubbles were simulated with solid spheres or disks generally showed that the increase in resistance was in broad agreement with the predictions shown in Figure 3.2.
Chapter 8 – Conclusions From Relevant Studies

8.1 Summary of Relevant Studies

The purpose of this chapter is to consolidate the conclusions from the relevant studies discussed in the preceding chapters, and to provide a justification for the work to follow.

The measurements on industrial cells confirm that bubbles can have a significant effect on cell performance, both in terms of cell voltage and current efficiency. It appears that increasing ohmic resistance in the electrolyte and increased activation polarisation are the main mechanisms by which bubbles have an effect. It appears that although bubbles do cause waves in the electrolyte/metal interface, the subsequent effect on resistance is relatively small.

Laboratory and physical modelling studies illustrate the high sensitivity of bubble behaviour to electrolysis conditions. In laboratory studies, various anode materials, including different types of graphite, have been observed to significantly affect bubble size, bubble layer thickness and the variation in cell voltage. In physical modelling studies, modification of the liquid used to simulate the electrolyte has shown that surface tension significantly affects bubble behaviour. This sensitivity is a serious issue for studying bubble behaviour in aluminium reduction cells, as it means that it is very difficult to ensure that the laboratory or physical modelling study is representative of an industrial cell.

A somewhat surprising observation from laboratory studies is that higher current density can result in lower bubble layer thickness, because the higher current density results in faster bubble release. However, it is unknown whether this trend applies in industrial cells, because the bubble coalescence and fluid mechanics may be significantly different at a larger scale.

The focus of this thesis is on how anode geometry could be improved (e.g. introduce a slot) to reduce the resistance due to bubbles. It is almost certain that investigations of this
type must be undertaken at full-scale to maintain geometric similarity. This really precludes ‘traditional’ laboratory studies on small anodes (e.g. Ø30 mm).

Physical modelling can be conducted at full-scale without too many issues, provided the bubbles are mechanically generated. However, it is risky to apply results from non-validated physical models to industrial cells, given the high sensitivity of results to experimental conditions. In fact, it is concluded that the risks of this approach are too high to be worthwhile.

Systematic evaluations of anode design in industrial cells are relatively time-consuming and expensive. However, cost is not the primary reason why such evaluations are not performed more often. The fundamental issue with measurements on industrial cells is that it is difficult to directly measure the effect of anode design on electrical resistance. Most smelters evaluate the effect of anode design via the anode noise, cell voltage and current efficiency, but these parameters are affected by numerous confounding variables such as alumina concentration, electrolyte temperature and ACD. It is not surprising that time-consuming, expensive studies that still only provide indirect measures of anode design performance are not popular!

It has been concluded from the relevant studies that the two aspects of bubble behaviour that must be considered are the effect on ohmic resistance and the effect on anodic polarisation. There have been remarkably few studies of these aspects in industrial cells, presumably because of the difficult experimental conditions, but they are possible. It is concluded that the best approach is to complete more extensive measurements of bubble resistance on industrial cells. These measurements may be sufficient to evaluate anode designs in-situ, or they may provide data against which physical models can be validated.

### 8.2 Planned Experimental Work

It was decided to concentrate on the effect of gas bubbles on ohmic resistance. The EIS technique described in Chapter 4.3.4 appears to offer some promise as a technique, and it has never been attempted on an industrial cell. In theory, an AC signal could be superimposed on the existing DC current in the industrial cell. One electrode could be connected to the anode rod or the anode itself, and the other could be connected to the
metal pad or the cathode collector bar. Thus the series resistance \( R_\Omega \) between these two points could be determined. As a reminder, the Randles equivalent circuit of an electrochemical cell (Figure 4.3) is reproduced below as Figure 8.1.

![Randles Equivalent Circuit](image)

Figure 8.1: Randles equivalent circuit as \( \omega \to \infty \), where Warburg impedance is negligible.

The issue is that EIS would probably not be suitable for measurements of series resistance on an industrial aluminium reduction cell because:

1. It would be difficult to produce an AC signal of the required magnitude.
2. The vigorous bubble release means that the system does not remain at steady state for the period of measurement (Snook et al. 2009).

Therefore a technique has to be developed that is based on EIS but addresses the two issues above. Section C describes the laboratory experiments undertaken to develop a technique suitable for measurement on industrial aluminium reduction cells. The proposed measurements were discussed with the Point Henry aluminium smelter, so the parameters for this smelter have been kept in mind during the development of the technique.

Determination of \( R_\Omega \) alone does not give the bubble resistance. However, if \( R_\Omega \) can also be determined in the absence of bubbles, then the resistance due to bubbles \( R_b \) can be determined (assuming all other sources of resistance remain unchanged between the two experiments) via:

\[
R_b = R_\Omega(\text{with bubbles}) - R_\Omega(\text{without bubbles})
\] (8.1)
$R_\Omega$ can only be determined in the absence of bubbles by switching off the DC current. Fortunately, the current only has to be switched off for the anode of interest, not the whole cell. This can be achieved by placing an insulator between the anode rod and the anode beam.
SECTION C:

DEVELOPMENT OF MEASUREMENT TECHNIQUE
Chapter 9 – Preliminary Experiments

9.1 Introduction

Before attempting to perform measurements on industrial cells, it was considered necessary to develop and test the proposed techniques in the laboratory. In this chapter, preliminary experiments using a range of possible techniques are described.

9.2 Electrochemical Impedance Spectroscopy

9.2.1 Introduction

The use of EIS to determine the series resistance of an electrochemical cell was described in Chapter 4.3.4. It was recognised that EIS would probably not be suitable for measurements of series resistance on an industrial aluminium reduction cell because:

1. It would be difficult to produce an AC signal of the required magnitude.
2. The vigorous bubble release means that the system does not remain at steady state for the period of measurement (Snook et al. 2009).

However some experiments were conducted using EIS to confirm that bubble resistance could be measured using a well-established technique. The results were not intended to be directly applicable to industrial aluminium reduction cells.

9.2.2 Experimental

Two aqueous systems were investigated; ZnSO₄ and KOH. The electrolysis of zinc was initially chosen because it is analogous to the production of aluminium in that a metal (zinc) is produced at the cathode and a gas (oxygen) is produced at the anode. The concentration was approximately 2M, although since the solution was repeatedly used in multiple experiments, the concentration was not tightly controlled. The half-cell reactions in this system are (E° is the standard potential):
Anode: \( \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \leftrightarrow 2\text{H}_2\text{O}(l) \quad E^\circ = +1.23 \text{ V} \) (9.1)

Cathode: \( \text{Zn}^{2+}(aq) + 2e^- \leftrightarrow \text{Zn}(s) \quad E^\circ = -0.76 \text{ V} \) (9.2)

And the overall cell reaction is:

\[ 2\text{ZnSO}_4(aq) + 2\text{H}_2\text{O}(l) \leftrightarrow 2\text{Zn}(s) + \text{O}_2(g) + 4\text{HSO}_4(aq) \quad E = -1.99 \text{ V} \] (9.3)

The results using \( \text{ZnSO}_4 \) raised the possibility that the deposition of zinc onto the cathode may have been changing the surface conditions of the cathode and affecting the overall ohmic resistance. To eliminate this possibility, the electrolyte was changed to 1M KOH. The half-cell reactions in this system are:

Anode: \( \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \leftrightarrow 4\text{OH}^-(aq) \quad E^\circ = +0.40 \text{ V} \) (9.4)

Cathode: \( 2\text{H}_2\text{O}(l) + 2e^- \leftrightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad E^\circ = -0.83 \text{ V} \) (9.5)

And the overall cell reaction is:

\[ 2\text{H}_2\text{O}(l) \leftrightarrow \text{O}_2(g) + 2\text{H}_2(g) \quad E = -1.23 \text{ V} \] (9.6)

i.e. Water is being decomposed to oxygen gas at the anode and hydrogen gas at the cathode. The electrode surfaces should therefore remain unchanged. This system is different to an industrial aluminium reduction in cell in that gas is produced at both electrodes, but this is irrelevant when considering the capability of a technique to measure the effect of bubbles on resistance.

Several different electrodes were used:

- A graphite electrode with a single 6 cm x 3 cm exposed face with a copper rod inserted to provide electrical contact. These were prepared by mounting a graphite block in epoxy and sectioning it in half, producing two electrodes. These were intended to be analogous to carbon anodes in industrial aluminium reduction cells;
- A 12 cm x 4 cm zinc plate, with immersion depth typically ~8 cm;
- A 9 cm x 1.4 cm platinum plate, with immersion depth typically ~4 cm;
A number of systems were investigated, as shown in Table 9.1.

Table 9.1: Systems where EIS was tested as a method of measuring resistance due to bubbles.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Anode</th>
<th>Cathode</th>
<th>Sets of Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄</td>
<td>Graphite</td>
<td>Graphite</td>
<td>2</td>
</tr>
<tr>
<td>ZnSO₄</td>
<td>Platinum</td>
<td>Zinc</td>
<td>1</td>
</tr>
<tr>
<td>KOH</td>
<td>Platinum</td>
<td>Platinum</td>
<td>3</td>
</tr>
</tbody>
</table>

Both electrodes were arranged vertically in all experiments for ease of experimentation. This is different to an industrial aluminium reduction cell, where the electrodes are horizontal, but fundamentally does not change the fact that bubbles will be present in the ACD and increase the ohmic resistance.

A Solartron 1286 potentiostat was used to apply a signal, and a Solartron 1255A Frequency Response Analyzer (0.2% accuracy) was used to measure the voltage. The negative terminal of the potentiostat was connected to one electrode and the positive terminal was connected to the other electrode. This experimental setup meant that the determined value of $R_\Omega$ represented not just the electrolyte and bubble resistance, but also any additional ohmic resistance in the electrodes and leads.

A set of EIS experiments consisted of the following:

1. A constant current or voltage was supplied to produce a significant number of bubbles on one or both electrodes, and the voltage was measured;
2. Three EIS measurements were conducted where there was no DC signal supplied, i.e. the electrodes were simply immersed in the electrolyte and no electrochemical reaction was taking place. The AC signal had an amplitude of 10 mV and was supplied at frequencies from 1 MHz down to 10 Hz, at 12 frequencies within each order of magnitude, i.e. 61 frequencies in total;
3. Three EIS measurements were conducted where a DC signal approximately equal to the DC voltage measured in step (1) was also applied, i.e. an electrochemical reaction was taking place and hence bubbles were being produced. The AC signal was identical to that applied in step (2).
9.2.3 Results

The most repeatable results were obtained with the system involving a 1M KOH electrolyte, platinum anode and platinum cathode, so only these results are described in detail here.

It was experimentally determined that an applied voltage of 3 V between the two electrodes was sufficient to produce an electrochemical reaction and a suitably large number of H₂ and O₂ bubbles.

A Nyquist plot for when there was no DC signal (i.e. no bubbles) is shown in Figure 9.1a. Recall from Figure 4.4 that the series resistance $R_\Omega$ is the value of $Z'$ where $Z'' = 0$. The intersection of the data with the $Z'' = 0$ horizontal axis is too difficult to determine from Figure 9.1a, so this region of the data is expanded in Figure 9.1b. It can be seen that $R_\Omega$ is approximately 1.65 Ω for each of the three experiments. In fact, using interpolation between the two points immediately greater and less than $Z'' = 0$ gives values of 1.653 Ω, 1.653 Ω and 1.652 Ω, for an average of 1.652 Ω, i.e. $R_\Omega = 1.652 \Omega$.

Nyquist plots of the results when the DC signal was applied are shown in Figure 9.2. For this data, again using interpolation, $R_\Omega = 1.661 \Omega$. Thus $R_\Omega$ has increased by 0.008 Ω, or 0.49%, after the application of a constant 3 V. The H₂ and O₂ bubbles are possibly a cause of this increase in resistance, but other possible causes cannot be discounted.

Two further similar sets of experiments were performed, and the results are summarised in Table 9.2. Each value of $R_\Omega$ is the average of three runs, as described above. All data was as consistent as shown in Figure 9.1b and Figure 9.2b, so the results were very repeatable within a set of three experiments. The absolute differences listed in Table 9.2 were confident to >98% using the Mood Median² test. The percentage increase in resistance was greater for the smaller ACD, as expected. The frequency at which the series resistance was determined ranged from 30 to 70 kHz.

---

¹ The apparent discrepancy that 1.661 Ω − 1.652 Ω = 0.008 Ω is due to rounding.

² Used instead of a t-test, because of only three points in each set of data
The results show that the results were not repeatable between the sets of three experiments. This is not surprising, because it was difficult to accurately control the immersion depth of the electrodes, and also the conductivity of the electrolyte may have changed slightly. The platinum electrodes were very malleable, which could have also resulted in a variable ACD.

Table 9.2: Summary of EIS results with 1M KOH electrolyte, platinum cathode and platinum anode.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Date</th>
<th>ACD (mm)</th>
<th>$R_\Omega$ (Ω)</th>
<th>Increase</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>No DC</td>
<td>DC Applied</td>
<td>Absolute (Ω)</td>
</tr>
<tr>
<td>1</td>
<td>20/7/07</td>
<td>22</td>
<td>1.652</td>
<td>1.661</td>
<td>0.008</td>
</tr>
<tr>
<td>2</td>
<td>25/7/07</td>
<td>22</td>
<td>1.998</td>
<td>2.003</td>
<td>0.005</td>
</tr>
<tr>
<td>3</td>
<td>3/8/07</td>
<td>7</td>
<td>0.692</td>
<td>0.704</td>
<td>0.013</td>
</tr>
</tbody>
</table>

For comparison, Nyquist plots for the experiments conducted using a ZnSO$_4$ electrolyte, platinum anode and zinc cathodes are shown in Figure 9.3. The results were repeatable when no DC signal was applied, but not repeatable when a DC signal was applied. Also the series resistance decreased with the application of a DC signal, rather than increase as might be expected from a contribution of bubbles. Possible reasons are (1) generation of H$^+$ ions increased the conductivity of the electrolyte, and (2) the deposition of zinc onto the cathode changed the ohmic resistance of the system.

Overall, the EIS experiments confirmed that an electrochemical reaction can produce a consistent increase in the series resistance $R_\Omega$ for a given experimental setup, but other effects can confound the results.
Figure 9.1: Nyquist plot for electrolysis of KOH, when no electrochemical reaction was taking place.
Figure 9.2: Nyquist plot for electrolysis of KOH, when electrochemical reaction was taking place.
Chapter 9 – Preliminary Experiments

(a) When no electrochemical reaction was taking place

(b) When electrochemical reaction was taking place

Figure 9.3: Nyquist plot for electrolysis of ZnSO₄ (region around $Z' = 0$).
9.3 **FFT on Battery-Generated Signal through an Anode Rod**

9.3.1 **Introduction**

It was recognised in Chapter 9.2.1 that EIS would be unsuitable for measuring series resistance on an industrial aluminium reduction cell. It was identified that the requirements of the technique were:

1. Able to be performed at high currents such that the measurement could produce a measurable voltage in an aluminium reduction cell, which has very low resistance;
2. The measurements can be performed very rapidly (>10 Hz) so that the measurement is complete before the system being measured has time to change.

Recently, a technique has been developed that enables the second requirement to be satisfied (Snook et al. 2009). This Fast Fourier Transform Current Pulse (FFTCP) technique utilises the fact that any wave can be considered as being composed of a series of superimposed sine waves of different frequencies, magnitudes and phases. The FFTCP involves applying a bipolar square current pulse, measuring the voltage pulse, and using the FFT algorithm to treat the current and voltage pulses to produce a dynamic electrochemical impedance spectrum. At each frequency, Equations (4.1) to (4.4) can be used to calculate the real and imaginary impedance, and hence produce a Nyquist plot.

This chapter describes the experiments used to test whether the FFTCP technique could potentially be applied to an aluminium reduction cell. The tests were conducted on a dummy electrical circuit designed to represent part of an aluminium reduction cell.

9.3.2 **Experimental**

A 1.8 m anode rod was obtained from the Point Henry smelter, primarily to enable electrical connection mechanisms to be considered for future measurements on an industrial cell. The copper rod had a large cross-section (7.0 cm x 7.5 cm) and a high conductivity (~6 x 10^7 S.m^-1), so it had a very low resistance: 6 µΩ. To be detectable, it was considered that the injected current would have to produce 10 mV along the length of the anode rod, which would require a current of 1750 A, which is too high to be achieved in a laboratory setting. Therefore an additional 1 mΩ resistor was placed in the circuit;
only 10 A was required to produce a voltage of 10 mV across this resistor. The wires were rated to least 180 A continuous. The 1 mΩ resistor could be considered to be simulating the resistive circuit in the cell comprising the anode, bath and metal.

A schematic of the electric circuit is shown in Figure 9.4. The entire circuit was resistive, i.e. all the energy produced by the power source was dissipated as heat by the electronic load, resistor, anode rod and wires. The actual experimental setup is shown in Figure 9.5.

Initial experiments were conducted with 3 A and 40 A power sources, to gain an understanding of the operation of the electronic load. The main experiments were conducted with an Optima red-top 34-8002-002 sealed lead-acid battery (similar to a car battery) to provide current injection. The battery had a maximum voltage of 12.8 V and a cranking amps (CA) of 1000 A, i.e. it could supply 1000 A for at least 30 seconds and still maintain at least 1.2 V for each of the six cells in the battery (i.e. 7.2 V total). The battery had a C/20 capacity of 50 Ah (could supply 2.5 A for 20h).

A WCL488 Electronic Load was used to modulate the current from the battery so that a controlled current (e.g. a square wave) was applied to the anode rod and 1 mΩ resistor. The electronic load could handle a maximum voltage of 100 V, a maximum current of 1000 A and a maximum power of 12 kW. When the electronic load was off, the electrical circuit was not completed within the electronic load so there was no current flowing through the overall circuit.

A hazard of this experimental setup was that the battery was always ‘on’ when it was connected in circuit. Currents up to 1000 A could be produced, which would produce a lot of heat. It is only the electronic load that controls the flow of current. If the electronic load is switched to a short circuit then the battery will immediately generate 1000 A through the circuit. Initial tests confirmed that the electronic load could be used to switch current flow on and off in a controlled manner, by setting the maximum current prior to connecting the circuit within the electronic load. For the experiments themselves, the electronic load was operated such that the heat generated was limited, using either low currents or short times.
The aim was to apply as large a current at as high a frequency as possible for a specific length of time. The current and frequency were gradually increased to a combination of 95 A at 500 Hz. It was a rectangular wave with a 10% duty cycle, i.e. the current was 95 A for 200 µs followed by 0 A for 1800 µs.
The voltage across the 1 mΩ resistor was measured using a LeCroy Waverunner LT342 digital oscilloscope.

It was mentioned in Chapter 8 that one of the requirements for the measurement technique is current measurement. Current can be determined by measuring the voltage across a known resistance or the magnetic field induced by an electric current. This is routinely done on industrial cells, however, for the proposed measurement technique the current must be measured at high frequency (kHz and greater). For these experiments, the current was measured using a LEM PR50 Universal 50 MHz Current Probe (Figure 9.6). This probe can measure currents up to 50 A at frequencies up to 50 MHz. The probe was connected to the oscilloscope to record the data. Voltage and current were recorded at 2.5 MHz.

Figure 9.6: LEM PR50 Universal 50 MHz Current Probe.

A constraint of the current probe is that the maximum size of the conductor that can be measured is 5 mm x 5 mm, which is thinner than the wire used in these experiments. The solution was to separate the strands of the main wire in the electrical circuit. The wire consisted of 19 strands, and three strands were separated from the remaining 16 and passed through the current probe. The current through these three strands could now be measured directly, and the overall current was determined by multiplying the measured current by 19/3.
9.3.3 Results

The desired current and voltage, and actual current and actual voltage, for one pulse are shown in Figure 9.7. The desired voltage is calculated from the desired current and assumes the resistance is the specified 1 mΩ. The actual current took ~50 µs to reach the target value of 95 A, and there was significant overshoot. It appears that the electronic load was incapable of switching at the required rate.

FFT was used to transform the current and voltage data from the time domain to the frequency domain, using 4096 data points collected at 2.5 MHz. The results of the FFT transforms are shown in Figure 9.8. This shows that the magnitude of the current and voltage decrease significantly with frequency, as expected. The effect on the calculation of the impedance is shown in Figure 9.9. The magnitude of the impedance appears sensible up to ~30 kHz. At higher frequencies the data becomes extremely scattered, presumably because the current and voltage are so small (0.09 A and 0.2 mV at 30 kHz) that errors in the calculation of the impedance become significant. This may be insufficient for measurements on industrial cells: recall that in the EIS experiments on a 1M KOH solution the frequency at which the series resistance was determined was 30-70 kHz (Chapter 9.2.3).

It is believed that the low magnitudes of the high frequency components are due to the measured current not being sufficiently ‘square’, i.e. it takes too long to rise from zero to the target value. This would probably be even more of a problem on the industrial cells where the injected current needs to be of a relatively large magnitude to be detectable.

A Nyquist plot of the data up to ~25 kHz is shown in Figure 9.10, which indicates that the series resistance $R_Ω$ was approximately 0.6 mΩ, i.e. the 1 mΩ resistor was measured as having a resistance of 0.6 mΩ. This suggests that there are some confounding factors. This is in fact obvious because, for a pure resistor, the imaginary impedance $Z''$ should equal zero at all frequencies. The fact that $Z'' \neq 0$ in Figure 9.10 suggests that there is some capacitance and/or inductance in the system in the resistor being measured. As described in Chapter 4.3.4, it is not unexpected to encounter inductance when using high frequency AC signals.
Figure 9.7: One pulse of rectangular wave of 95A / 500 Hz / 10% duty cycle. Data for the 4096 points used for the FFT is shown.
Chapter 9 – Preliminary Experiments

Figure 9.8: FFT transforms of current and voltage to the frequency domain.

(a) Desired current and voltage, assuming 1 mΩ resistance

(b) Actual current and voltage
Figure 9.9: Magnitude of the impedance $|Z|$ as a function of frequency.

Figure 9.10: Nyquist plot for frequencies up to ~25 kHz.
9.4 **FFT on Capacitor-Generated Pulse through a Resistor**

9.4.1 **Introduction**

A way of increasing the relative magnitude of the impedance at high frequencies is to produce a sharper rise in the current, i.e. a ‘squerer’ wave. The electronic load was incapable of switching any faster, so a new method was needed to produce a current.

A capacitor can discharge extremely quickly and can also produce high current (100s or even 1000s of Amperes), although only for a very short time. Thus a capacitor was investigated as a method of injecting additional charge, replacing the 12 V battery used in Chapter 9.3.

The simplest test was to use a capacitor to inject charge into a resistor of known resistance and use FFT to calculate the impedance of the resistor. It was realised that there was no need to incorporate the anode rod as part of the circuit, so it was not used again.

9.4.2 **Experimental**

A circuit where $R_\Omega$ was known was constructed as shown in Figure 9.11. When the switch was open, the voltage source $V_g$ charged the 40 $\mu$F capacitor. When the switch was closed, the charge stored in the 40 $\mu$F capacitor rapidly discharged through the $R_1$ and $R_\Omega$ resistors. The current $I_T$ and voltage $V_T$ were measured using the same LEM PR50 Universal 50 MHz Current Probe and LeCroy Waverunner LT342 oscilloscope as in the previous work using the electronic load (Chapter 9.3.2). They were recorded at 250 MHz, as it was thought best to maximise this frequency. The FFT was used to transform $I_T$ and $V_T$ to the frequency domain so that the equivalent series resistance $R_\Omega$ could be obtained using a Nyquist plot.

Two tests are reported here, with experimental conditions shown in Table 9.3. In Test 1, $R_\Omega$ was a calibrated 1 m$\Omega$ resistor. In Test 2, $R_\Omega$ was 77 mm of calibrated 2.6 $\Omega$/m high resistance wire, which gave a total resistance of 0.2 $\Omega$. The expected maximum current $I_T$ is the quotient of $V_g$ and $(R_1 + R_\Omega)$, and the expected maximum voltage $V_T$ is the product of $I_T$ and $R_\Omega$. 
Chapter 9 – Preliminary Experiments

Figure 9.11: Electrical circuit used to test use of capacitor as source of current to measure equivalent series resistance $R_\Omega$.

Table 9.3: Experimental conditions for testing use of capacitor as source of current to measure equivalent series resistance $R_\Omega$.

<table>
<thead>
<tr>
<th>Test</th>
<th>$V_g$ (V)</th>
<th>$R_1$ (Ω)</th>
<th>$R_\Omega$ (Ω)</th>
<th>Frequency of Measurement (MHz)</th>
<th>Expected Max Current $I_T$ (A)</th>
<th>Expected Max Voltage $V_T$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70</td>
<td>2</td>
<td>0.001</td>
<td>250</td>
<td>35</td>
<td>0.035</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>2</td>
<td>0.2</td>
<td>250</td>
<td>32</td>
<td>6.4</td>
</tr>
</tbody>
</table>

9.4.3 Results

A section of the current and voltage data (4096 points) for Test 1 is shown in Figure 9.12. The maximum current was 30 A, reasonably close to the expected value of 35 A (Table 9.3). Importantly, the maximum current was reached in $\sim$5 µs, much quicker than when using the electronic load to modulate the current from a 12 V battery ($\sim$50 µs – Chapter 9.3.3). Thus the capacitor was effective in producing a current with a shorter rise time.

The voltage trend should match the current trend, but this clearly was not the case in the first 5 µs. The maximum voltage was 0.25 V, an order of magnitude higher than the expected 0.035 V. It is possible that inductance in the 1 mΩ resistor induced a relatively large voltage to resist the large change in current.

For the 10 µs from $t = 5$ µs to $t = 15$ µs, the voltage trend did match the current trend, and the quotient of the voltage and current is $\sim$1 mΩ, as expected from the value of $R_\Omega$. The current and voltage appear to decay slowly (e.g. the current decays to $\sim$27 A at $t = 15$ µs),
and this can be checked given that for current flowing through a single capacitor \(C\) and resistor \(R\):

\[
I = I_e \left( \frac{t}{RC} \right) \quad (9.7)
\]

\[
V = V_i e^{- \frac{t}{RC}} \quad (9.8)
\]

Where:  
\(I_i\) = initial current  
\(V_i\) = initial voltage

The \(RC\) product is known as the time constant of a capacitor. Using Equation (9.7) for the 10 \(\mu\)s from \(t = 5 \mu\)s to \(t = 15 \mu\)s:

\[
I = 30e^{- \frac{10\times10^{-6}}{(2+0.001)\times40\times10^{-6}}} = 26 \text{ A}
\]

This is very close to the current at \(t = 15 \mu\)s shown in Figure 9.12, i.e. from \(t = 5 \mu\)s onwards, the current and voltage exhibited the expected trend.

A section of the current and voltage data (4096 points) for Test 2 is shown in Figure 9.13. The maximum current was \(~31\) A and the maximum voltage was \(~6.3\) V. These are both close to the expected values (Table 9.3), and the voltage showed a similar pattern to the current. This suggests that inductance had largely been eliminated in this experiment, and is believed to be because the inductance-to-resistance ratio of the high resistance wire is much lower than for the 1 m\(\Omega\) resistor. Although \(R_\Omega\) is much larger in Test 2, the rate of decay of the current and voltage is similar in Test 1 and Test 2 because the total resistance is relatively unchanged, as it is dominated by the \(R_1\) resistor.

The FFT transforms of current and voltage for Test 2 are shown in Figure 9.14 and the Nyquist plot for frequencies up to 2 MHz is shown in Figure 9.15. The Nyquist plot is scattered and \(Z' = 0\) at three frequencies, which is unsuitable for determining \(R_\Omega\). However, the actual value of \(R_\Omega\) is 0.2 \(\Omega\), and the values of \(Z'\) when \(Z' = 0\) are not dissimilar to this, so this is some evidence using a capacitor to inject a current may allow
the series resistance to be determined. The Nyquist plot of a pure resistor should be a single point, so the presence of an imaginary component suggests that there is still some capacitance and/or inductance in the system.

Figure 9.12: Current and voltage for Test 1; $R_\Omega = 1 \text{ m}\Omega$.

Figure 9.13: Current and voltage for Test 2; $R_\Omega = 0.2 \text{ }\Omega$. 
Figure 9.14: FFT transforms of current and voltage for Test 2; $R_{\Omega} = 0.2 \, \Omega$.

Figure 9.15: Nyquist plot for frequencies up to 2 MHz for Test 2; $R_{\Omega} = 0.2 \, \Omega$. 

9.5 **FFT on Capacitor-Generated Pulse through a Randles Equivalent Circuit**

9.5.1 **Introduction**

The next level of complexity is to use a capacitor to inject charge into a circuit that represents an electrochemical cell. These tests were performed using a Randles equivalent circuit that had been constructed for some related work (Snook et al. 2008).

9.5.2 **Experimental**

The Randles equivalent circuit (Figure 4.3) replaced the single $R_\Omega$ resistor in Figure 9.11, as shown in Figure 9.16. This circuit had the advantage that the resistances $R_\Omega$ and $R_{ct}$ and the capacitor $C_{dl}$ were known to reasonable accuracy and could be varied.

![Figure 9.16: Electrical circuit used to test use of capacitor as source of current to measure series resistance $R_\Omega$.](image)

When the switch was closed, the charge stored in the 40 µF capacitor rapidly discharged through the $R_1$ resistor and the Randles equivalent circuit. Initially, all of the current $I_T$ passes through the capacitor $C_{dl}$ because it acts as a short circuit. As the voltage across $C_{dl}$ increases, a higher proportion of $I_T$ passes through the resistor $R_{ct}$. The current $I_T$ and voltage $V_T$ were again measured using the LEM PR50 Universal 50 MHz Current Probe and LeCroy Waverunner LT342 oscilloscope respectively.

Three tests are reported here, with experimental conditions shown in Table 9.4. Both $R_\Omega$ and $R_{ct}$ were accurate to ±10%. Two different capacitances $C_{dl}$ were used; 30 µF and 1 mF. The frequency of measurement was 0.5 MHz, compared to 250 MHz used for the
resistor in the previous section. This is because it was realised that 250 MHz was too high to obtain FFT data in the desired 10-100 kHz range (from Chapter 9.2.3).

Table 9.4: Experimental conditions for testing use of capacitor as source of current to measure series resistance $R_\Omega$.

<table>
<thead>
<tr>
<th>Test</th>
<th>$V_g$ (V)</th>
<th>$R_1$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{dl}$ (mF)</th>
<th>$R_\Omega$ (Ω)</th>
<th>Frequency of Measurement (MHz)</th>
<th>Expected Max Current $I_T$ (A)</th>
<th>Expected Max Voltage $V_T$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>60</td>
<td>1</td>
<td>100</td>
<td>0.03</td>
<td>1</td>
<td>0.5</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>1</td>
<td>100</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>1</td>
<td>100</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

9.5.3 Results

A section of the current and voltage data (512 points) for Test 3 is shown in Figure 9.17a. The maximum current and voltage are approximately in line with that expected from Table 9.4. The current decays close to zero but the voltage does not. Equation (9.7) cannot be used to calculate the expected decay of the current, because the circuit is more complex than a single capacitor $C$ and resistor $R$. The Nyquist plot (Figure 9.17b) does not allow the series resistance $R_\Omega$ to be determined because $Z' = 0$ at multiple frequencies.

Similar current and voltage data for Test 4 is shown in Figure 9.18a. Again the maximum current and voltage are approximately in line with that expected from Table 9.4. The current and voltage decay in a similar fashion, although only the current decays close to zero. The voltage decay is in great contrast to Figure 9.17a, and is because a capacitor with a higher capacitance discharges more quickly ($C_{dl} = 1$ mF compared to 30 µF in Test 3). The series resistance $R_\Omega$ is 1.1 Ω as determined from the Nyquist plot (Figure 9.18b). This is the value of $R_\Omega$ (within the quoted accuracy of 1 Ω ±10%).

Similar current and voltage data for Test 5 is shown in Figure 9.19a. Compared to Tests 3 and 4, the maximum voltage is higher and the maximum current is lower, as expected from Table 9.4. The Nyquist plot for Test 5 is shown in Figure 9.19b, and the series resistance is determined as ~2.3 Ω, which is not dissimilar to the actual value of 2 Ω ±10%.
The Nyquist plots for Tests 4 and 5 exhibit significantly different patterns. The reason for this is unknown, and it was not worth investigating at this preliminary stage of investigation.

![Figure 9.17](image-url)

(a) Current and voltage

(b) Nyquist plot for frequencies up to 40 kHz

Figure 9.17: Measurements for Test 3; $R_f = 1 \ \Omega$, $R_{ct} = 100 \ \Omega$, $C_{dl} = 30 \ \mu F$, $R_{\Omega} = 1 \ \Omega$. 
Figure 9.18: Measurements for Test 4; $R_f = 1 \, \Omega$, $R_{ct} = 100 \, \Omega$, $C_{dl} = 1 \, \text{mF}$, $R_\Omega = 1 \, \Omega$. 
Figure 9.19: Measurements for Test 5; $R_I = 1 \ \Omega$, $R_{ct} = 100 \ \Omega$, $C_{dl} = 1 \ \text{mF}$, $R_\Omega = 2 \ \Omega$. 

(a) Current and voltage 

(b) Nyquist plot for frequencies up to 40 kHz
9.6 Conclusions

The EIS experiments confirmed that the series resistance can be determined, although it was recognised that this technique would not be suitable for measurements on industrial aluminium reduction cells, because insufficient currents could be produced and the system does not remain at steady state for the period of measurement.

The experiments using a 7.2 V battery to generate a rectangular wave of 95A / 500 Hz again showed that the series resistance could be measured. However this is also unlikely to be effective on industrial aluminium reduction cells because the rise time of current is too long (produce low magnitudes of high frequency components of current and voltage)

The results using a capacitor to inject charge showed that a current with a sharp rise time could be produced, which means that the high frequency components in the FFT transforms are relatively large. This suggests that the use of a capacitor to inject charge into an anode rod to measure the series resistance may be feasible.

It was also found that the capacitance $C_{dl}$ in a Randles equivalent circuit affects whether it is possible to use this technique. Presumably, the resistances $R_{\Omega}$ and $R_{ct}$ could also have an effect.

Therefore a greater understanding of $C_{dl}$, $R_{\Omega}$ and $R_{ct}$, and their effect on the measured current $I_T$ and voltage $V_T$, is required before this method of measuring the series resistance $R_{\Omega}$ on an industrial aluminium reduction cell can be attempted with confidence. This is explored in the next chapter.
CHAPTER 10 – CURRENT INJECTION USING A CAPACITOR - DEVELOPMENT

10.1 Introduction

In Chapter 9.4 it was concluded that a greater understanding of $C_{dl}$, $R_\Omega$ and $R_{ct}$ was required before the method of using a capacitor to inject charge into an anode rod on an industrial cell to determine the series resistance $R_\Omega$ could be attempted with confidence.

The purpose of this chapter is to demonstrate that smelter measurements are feasible, which requires:

1. An understanding of the likely values of $C_{dl}$, $R_\Omega$ and $R_{ct}$ in an industrial cell;
2. An understanding of the constraints for the measurements;
3. A demonstration that the technique will work under these conditions.

10.2 Industrial Aluminium Reduction Cell Parameters

$R_\Omega$ can be estimated from the voltage components and geometry of the cell. If it is assumed that the measurements will be conducted between a point on the anode rod and another point on the cathode collector bar, then $R_\Omega$ comprises the resistance of the rod, anode, electrolyte, metal, cathode and collector bar. The approximate total voltage for these regions can be estimated as 2.3 V (Figure 1.3). At the Point Henry smelter, where measurements are proposed, the current is 185 kA and there are 24 anodes, hence each anode nominally carries 7.7 kA. Therefore $R_\Omega = \frac{2.3}{7700} = 0.3 \, \text{m}\Omega$.

A number of laboratory studies have investigated $R_{ct}$ and $C_{dl}$. Capacitance is strongly dependent on surface area, so the nature of the anode material (e.g. porosity) can have a strong effect. Therefore the values of $C_{dl}$ obtained from studies on baked anode carbons are probably more relevant than those from other carbons such as graphite.

EIS has been used to investigate a number of carbons, including baked anode carbon, at current densities up to 0.15 A.cm$^{-2}$ (Thonstad 1970). $C_{dl}$ was found to be $350 \, \mu\text{F.cm}^{-2}$.
(range 150-600 µF.cm\(^{-2}\)) for the baked carbon. \(R_{ct}\) was found to be small and it was hypothesised that it may have a value of <0.03 Ω.

EIS has also been used to investigate the double layer capacitance of three anode materials: pyrolytic graphite, spectral pure graphite and baked carbon, at a range of current densities (Jarek and Orman 1985). Each material was machined into rods and fitted into a BN tube, so that only the horizontal downward face was exposed. \(C_{dl}\) was found to be 220 µF.cm\(^{-2}\) for baked carbon (157-284 µF.cm\(^{-2}\) at 0.7 A.cm\(^{-2}\) and 119-253 µF.cm\(^{-2}\) at 1.2 A.cm\(^{-2}\)). The results also suggested that \(R_{ct}\) was very small.

Similar EIS measurements were conducted on anodes constructed from pyrolytic graphite and spectral pure graphite, at current densities up to 0.6 A.cm\(^{-2}\) (Kisza, Thonstad, and Eidet 1996). The total charge-transfer resistance \(R_{ct}\) was found to be ~0.02 Ω at the highest current densities.

The results from the above studies are reasonably consistent and sufficient to provide a guide to the likely values of \(R_Ω\), \(R_{ct}\) and \(C_{dl}\) in an industrial cell, which are summarised in Table 10.1.

Table 10.1: Likely values of \(R_Ω\), \(R_{ct}\) and \(C_{dl}\) in an industrial aluminium reduction cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Likely Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_Ω)</td>
<td>mΩ</td>
<td>0.3</td>
</tr>
<tr>
<td>(R_{ct})</td>
<td>Ω</td>
<td>0.01</td>
</tr>
<tr>
<td>(C_{dl})</td>
<td>µF.cm(^{-2})</td>
<td>400</td>
</tr>
</tbody>
</table>

### 10.3 Constraints

There are three types of constraints for the measurements:

1. The current, voltage and energy produced must be practical from an engineering point of view, and safe. The energy supplied in the pulse must be low enough to avoid any excessive heat generation. This is unlikely to be an issue as a capacitor actually stores relatively little charge;

2. The current \(I_T\) and voltage \(V_T\) produced by the injected charge must be detectable;
3. The FFT transforms of the current $I_T$ and voltage $V_T$ ($I_{Tz}$ and $V_{Tz}$ respectively) must allow the series resistance to be calculated.

Some of these are listed in Table 10.2.

Table 10.2: Constraints for injecting charge using a capacitor to measure series resistance.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Constraint</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_g$</td>
<td>&lt;100 V</td>
<td>Prefer an ultra-low voltage that is considered intrinsically safe to people</td>
</tr>
<tr>
<td>$C_g$</td>
<td>1 µF – 10 F</td>
<td>Must be a commercially obtainable capacitor</td>
</tr>
<tr>
<td>$E = \frac{C_g V_g^2}{2}$</td>
<td>&lt;1000 J</td>
<td>Limit heat generation</td>
</tr>
<tr>
<td>$n$</td>
<td>$2^n$</td>
<td>Must be a power of 2 to perform FFT</td>
</tr>
<tr>
<td>$I_T$</td>
<td>No limit</td>
<td>Believe that instantaneous current is not a constraint for safety reasons. However large current is probably more difficult to achieve instantaneously, due to inductance in capacitor</td>
</tr>
</tbody>
</table>

### 10.4 Measurement Parameters

In addition to $R_\Omega$, $R_{ct}$ and $C_{dl}$, there are another four parameters related to the measurements that can be directly varied:

- The capacitance $C_g$ of the capacitor used to inject the charge;
- The voltage $V_g$ of the capacitor used to inject the charge;
- The sampling frequency $f_s$;
- The number of data points collected $n$.

### 10.5 Method Development

The total of seven parameters meant that it was impractical to construct and test the large number of possible circuits, so equations for $I_T$ and $V_T$ were derived so that data such as Figure 9.17 could be obtained solely via calculation. This allows Nyquist plots to be obtained for a range of values of $R_\Omega$, $R_{ct}$, $C_{dl}$, $C_g$ and $V_g$. 
Chapter 10 – Current Injection Using a Capacitor - Development

10.6 Single Capacitor Pulse – Ideal Circuit

10.6.1 Derivation of Equations

Figure 9.16 is simplified in Figure 10.1. The capacitor $C_g$ is charged to $V_g$. When the switch is closed, the capacitor $C_g$ discharges and produces a current $I_T$ through the remainder of the circuit. As $R_\Omega$, $R_{ct}$, $C_{dl}$, $C_g$ and $V_g$ are known, there are three unknowns; $V_T$, $I_{dl}$ and $I_{ct}$, which can be solved through three simultaneous equations. The derivation of Equation (10.1) for $I_T$ and Equation (10.2) for $V_T$ is shown in Appendix A.

Figure 10.1: Randles equivalent circuit as $\omega \rightarrow \infty$, with capacitor $C_g$ used to inject charge through remainder of circuit.

\[
I_T = \frac{k_1 k_2 C_g V_g}{k_1 - k_2} \left[ e^{k_1 t} (1 + k_1 R_{ct} C_{dl}) - e^{k_2 t} (1 + k_2 R_{ct} C_{dl}) \right] \tag{10.1}
\]

\[
V_T = \frac{k_1 k_2 C_g V_g}{k_1 - k_2} \left[ e^{k_1 t} (R_\Omega + R_{ct} + k_1 R_{ct} R_\Omega C_{dl}) - e^{k_2 t} (R_\Omega + R_{ct} + k_2 R_{ct} R_\Omega C_{dl}) \right] \tag{10.2}
\]

10.6.2 Experimental

The values investigated using Equations (10.1) and (10.2) are shown in Table 10.3. The values of $R_\Omega$, $R_{ct}$ and $C_{dl}$ are from Table 10.1 with $C_{dl} = 3$ F based on bottom anode dimensions of 140 cm x 60 cm. The values for $C_g$, $V_g$, $f_s$ and $n$ were based on a best judgement. Two additional values of $C_g$ were considered, as described in the Simulation Results below. The combination of $f_s$ and $n$ meant that the length of pulse being

\footnote{An attempt was made to include an inductor in the circuit shown in Figure 10.1 and derive the equations for the discharge of the capacitor as described below. However, this led to a third order differential equation that could not be solved.}
considered was 2.56 ms. The positive pulse was set to commence at \( t = 100 \mu s \), just so the data could be more easily visualised on a chart.

Table 10.3: Values evaluated using equations for \( I_T \) and \( V_T \) for single capacitor pulse

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<th>Other Values</th>
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<td>-</td>
</tr>
<tr>
<td></td>
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<td>( \Omega )</td>
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<td>-</td>
</tr>
<tr>
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<td>3</td>
<td>-</td>
</tr>
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<tr>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>-</td>
<td>256</td>
<td>-</td>
</tr>
</tbody>
</table>

10.6.3 Simulation Results

The calculated currents \( I_{ct} \), \( I_{dl} \) and \( I_T \) are shown for the base case in Figure 10.2, and the calculated voltages \( V_\Omega \), \( V_{ct} \) and \( V_T \) are shown in Figure 10.3. Recall that \( V_{ct} = V_{dl} \) because they are in parallel. Figure 10.2 shows that almost all of the current travels through the capacitor \( C_{dl} \) rather than the resistor \( R_{ct} \). Figure 10.3 shows that the charge injected from the capacitor \( C_g \) charges the capacitor \( C_{dl} \) until the voltages on the two capacitors are approximately equal in magnitude but opposite in sign (after 1000-1500 \( \mu s \)). Further discharging of the two capacitors is extremely slow.

The calculated current \( I_T \) and voltage \( V_T \) for a lower value of \( C_g \) (0.1 F) is shown in Figure 10.4a. Figure 10.4b is a reproduction of some data from Figure 10.2 and Figure 10.3. The effect of the lower value of \( C_g \) (Figure 10.4a) is that less charge is stored in the capacitor \( C_g \), so the voltage to which \( V_T \) and \( V_{ct} \) converge is lower.

The data in Figure 10.4 was transformed using FFT to produce 256 component waves of 391 Hz to 100 kHz, and Nyquist plots are shown in Figure 10.5. The Nyquist plots for both values of \( C_g \) exhibit an unusual pattern, although the values of \( Z' \) where \( Z'' = 0 \) are not dissimilar to the expected value of 0.3 m\( \Omega \). It would not be possible to use data of this form to accurately determine the value of \( R_\Omega \). Also shown is the predicted \( Z' \) and \( Z'' \) using Equations (4.5) and (4.6) for frequencies of 390 Hz to 100 kHz. These data are quite different to the semi-circle shown in Figure 4.4, in that only a small portion of the semi-circle is visible (one might expect to see a semi-circle with x-intercepts at \( Z' = 0.3 \) m\( \Omega \))
and at $0.3 + 10 = 10.3 \text{ m} \Omega$). This can be explained as follows. In Figure 4.4, the highest point of the semi-circle is at the point where the angular frequency $\omega$ is equal to $1/R_{ct}C_{dl}$. For the data presented here, this would be at $\omega = 1 / 0.01 \times 3 = 33 \text{ Hz}$. As the lowest component wave produced by the FFT is at $\omega = 390 \times 2\pi = 2500 \text{ Hz}$, most of the semi-circle is not visible.

Reasons for the unusual Nyquist plots from the simulated data can be investigated by considering the FFT in more detail. The FFT transforms the data from the time domain to the frequency domain. It is then possible to reconstruct the time series data back from the frequency domain data. The results of taking the first 100 frequencies of the current $I_{Tz}$ and voltage $V_{Tz}$ for the base case and summing them to produce time series is shown in Figure 10.6. These should exactly match the original time series data in Figure 10.4b. The data is similar, with the notable exception that the voltage returns close to zero at the end of the data in the reconstructed time series (indicated by the arrow in Figure 10.6). This is because the FFT assumes that the data starts and ends at zero.

This may be why the Nyquist plot does not produce data that is suitable for determining $R_{\Omega}$. It is possible that the current and voltage must both decay close to zero, because only then will the FFT function effectively. Allowing the voltage due to decay close to zero can be achieved by using a lower value of $C_g$ as shown in Figure 10.4a. The calculated current $I_T$ and voltage $V_T$ for an even lower value of $C_g (0.01 \text{ F})$ are shown in Figure 10.7. In this case, the voltage decays to $0.3\%$ of its original value, which could be considered close to zero. The Nyquist plot for this case is shown in Figure 10.8, and it appears more likely that the value of $R_{\Omega}$ could be accurately determined from this figure.

Another test of the method is that, for a Randles circuit, a plot of $-Z''$ against the inverse of the angular frequency ($\omega = 2\pi f$) should be a straight line, with its slope equal to the inverse of the capacitance $C_{dl}$ (Snook et al. 2007). Such a ‘capacitance plot’ for the transformed data from Figure 10.7 is shown in Figure 10.9. The data is clearly non-linear, which suggests that there are still issues with the time series data and its FFT. Perhaps this is because the data in Figure 10.7 is unusual in that it is a very short pulse followed by a relatively long time at almost zero.
This suggests that the method of using a low value of $C_g$ to ensure that the voltage decays close to zero by the end of the pulse may not be appropriate, and that an alternative method is required. A possible method is to inject a bipolar pulse, i.e. a positive pulse from a capacitor as described above, followed by a negative pulse provided from a capacitor charged to a negative voltage of the same magnitude. The sum of these two pulses may produce a final voltage relatively close to zero, and allow an appropriate FFT to be performed to allow the series resistance $R_\Omega$ to be determined from a Nyquist plot. The investigation of this method is described in the next section.
Figure 10.2: Calculated $I_{ct}$, $I_{dl}$ and $I_T$ for base case ($R_\Omega = 0.3$ m$\Omega$, $R_{ct} = 0.01$ $\Omega$, $C_{dl} = 3$ F, $C_g = 1$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$).

Figure 10.3: Calculated $V_\Omega$, $V_{ct}$ and $V_T$ for base case ($R_\Omega = 0.3$ m$\Omega$, $R_{ct} = 0.01$ $\Omega$, $C_{dl} = 3$ F, $C_g = 1$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$).
Figure 10.4: Calculated current $I_T$ and voltage $V_T$ for two values of $C_g$ ($R_\Omega = 0.3$ m$\Omega$, $R_{ct} = 0.01$ $\Omega$, $C_{dl} = 3$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$).
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Simulation Equations 4.5 and 4.6

(a) $C_g = 0.1 \text{ F}$

(b) $C_g = 1 \text{ F}$

Figure 10.5: Calculated Nyquist plot for two values of $C_g$ ($R_\Omega = 0.3 \text{ m}\Omega$, $R_{ct} = 0.01 \text{ \Omega}$, $C_{dl} = 3 \text{ F}$, $V_g = 1 \text{ V}$, $f_s = 100 \text{ kHz}$, $n = 256$).
Figure 10.6: Reconstruction of calculated current $I_T$ and voltage $V_T$ using first 100 frequencies of current $I_{Tz}$ and voltage $V_{Tz}$, for base case ($R_\Omega = 0.3$ m$\Omega$, $R_{ct} = 0.01$ $\Omega$, $C_{dl} = 3$ F, $C_g = 1$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$). Arrow highlights difference compared to original time series in Figure 10.4b.

Figure 10.7: Calculated current $I_T$ and voltage $V_T$ for lower value of $C_g$ ($R_\Omega = 0.3$ m$\Omega$, $R_{ct} = 0.01$ $\Omega$, $C_{dl} = 3$ F, $C_g = 0.01$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$).
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Figure 10.8: Calculated Nyquist plot for lower value of $C_g$ ($R_\Omega = 0.3$ m\(\Omega\), $R_{ct} = 0.01$ \(\Omega\), $C_{dl} = 3$ F, $C_g = 0.01$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$).

![Nyquist plot](image)

Figure 10.9: Calculated capacitance plot for lower value of $C_g$ ($R_\Omega = 0.3$ m\(\Omega\), $R_{ct} = 0.01$ \(\Omega\), $C_{dl} = 3$ F, $C_g = 0.01$ F, $V_g = 1$ V, $f_s = 100$ kHz, $n = 256$). Line is a linear line of regression.

![Capacitance plot](image)
10.7 Bipolar Capacitor Pulse – Ideal Circuit

10.7.1 Derivation of Equations

The theoretical circuit from Figure 10.1 was modified to that shown in Figure 10.10. When the switch connecting the capacitor charged to $V_g$ is closed, a current $I_T$ is produced through the remainder of the circuit. After a fixed period, this switch is opened and the switch connecting the capacitor charged to $-V_g$ is closed, producing a new current $I_T$ through the remainder of the circuit. This introduces an additional measurement parameter to the four shown in Table 10.3: the time between the positive and negative pulses $t_{gap}$. The equations for $I_T$ and $V_T$ can be solved in the same manner as performed previously in Chapter 10.6, however some modifications need to be made. The derivation of Equation (10.3) for $I_T$ and Equation (10.4) for $V_T$ is shown in Appendix B.

![Figure 10.10: Randles equivalent circuit as $\omega \to \infty$, with two capacitors $C_g$ used to inject charge through remainder of circuit.](image)

\[
I_T = \frac{1}{k_1 - k_2} \left[ k_1 e^{k_1 t} \left( k_2 \left( C_g V_g + q_{d0} \right) + \frac{q_{d0}}{R_g C_{dl}} \right) \left( 1 + k_1 R_{ct} C_{dl} \right) \right] - k_2 e^{k_2 t} \left[ k_1 \left( C_g V_g + q_{d0} \right) + \frac{q_{d0}}{R_{ct} C_{dl}} \left( 1 + k_2 R_{ct} C_{dl} \right) \right] \]  (10.3)

\[
V_T = \frac{1}{k_1 - k_2} \left[ k_1 e^{k_1 t} \left( k_2 \left( C_g V_g + q_{d0} \right) + \frac{q_{d0}}{R_g C_{dl}} \right) \left( R_\Omega + R_{ct} + k_1 R_{ct} R_\Omega C_{dl} \right) \right] - k_2 e^{k_2 t} \left[ k_1 \left( C_g V_g + q_{d0} \right) + \frac{q_{d0}}{R_{ct} C_{dl}} \left( R_\Omega + R_{ct} + k_2 R_{ct} R_\Omega C_{dl} \right) \right] \]  (10.4)
10.7.2 Experimental

The values investigated using Equations (10.3) and (10.4) were as per the single capacitor pulse, i.e. the base case values in Table 10.3. Initially, for the simple reason that it splits the single positive pulse approximately in half, $t_{gap}$ was set to be 1 ms. As previously, the positive pulse commenced at $t = 100 \mu s$.

10.7.3 Simulation Results

The calculated current $I_T$ and voltage $V_T$ for the bipolar pulse for the base case are shown in Figure 10.11b. The equivalent calculation for the single pulse (Figure 10.4b) is reproduced in Figure 10.11a for comparison. The voltage $V_T$ finishes much closer to zero for the bipolar pulse, as hoped. However, the Nyquist plot for the bipolar pulse (Figure 10.12) appears to be too scattered to allow the series resistance $R_\Omega$ to be determined.

The capacitance plot is shown in Figure 10.13. It is quite different from that for the single capacitor pulse (Figure 10.9) in that it exhibits a moderately linear trend. Based on a linear regression, the inverse of the slope is 2.9, quite close to the value of $C_{dl}$ (3 F).

The bipolar capacitor pulse produced a final voltage relatively close to zero, and the correct capacitance could be determined from the capacitance plot. These results suggested that the bipolar capacitor pulse was superior to the single capacitor pulse, although it was still not possible to determine the series resistance $R_\Omega$ from the Nyquist plot. It is possible that optimised measurement parameters may allow an appropriate FFT to be performed to allow the series resistance $R_\Omega$ to be determined from a Nyquist plot.
Figure 10.11: Calculated current $I_T$ and voltage $V_T$ for base case ($R_\Omega = 0.3 \text{ m}\Omega$, $R_{ct} = 0.01 \text{ \Omega}$, $C_{dl} = 3 \text{ F}$, $C_g = 1 \text{ F}$, $V_g = 1 \text{ V}$, $f_s = 100 \text{ kHz}$, $n = 256$).
Figure 10.12: Calculated Nyquist plot for bipolar pulse ($R_Ω = 0.3 \, \text{mΩ}$, $R_{ct} = 0.01 \, \Omega$, $C_{dl} = 3 \, \text{F}$, $C_g = 1 \, \text{F}$, $V_g = 1 \, \text{V}$, $f_s = 100 \, \text{kHz}$, $n = 256$, $t_{gap} = 1 \, \text{ms}$).

Figure 10.13: Calculated capacitance plot for bipolar pulse ($R_Ω = 0.3 \, \text{mΩ}$, $R_{ct} = 0.01 \, \Omega$, $C_{dl} = 3 \, \text{F}$, $C_g = 0.01 \, \text{F}$, $V_g = 1 \, \text{V}$, $f_s = 100 \, \text{kHz}$, $n = 256$, $t_{gap} = 1 \, \text{ms}$).
10.8 Bipolar Capacitor Pulse – Optimisation

There are five parameters \( (C_g, V_g, f_s, n, t_{gap}) \) that can be varied. A method of optimising these parameters for a given \( R_\Omega, R_{ct} \) and \( C_{dl} \), was required, rather than relying on trial and error.

Through investigation, using Equations (10.3) and (10.4) for \( I_T \) and \( V_T \), it was found that \( V_g \) is independent of the other factors, e.g. if \( V_g \) is increased by a factor of 10, then data such as that shown in Figure 10.11b also increases by a factor of 10, and the Nyquist plot (e.g. Figure 10.12) is unchanged. So \( V_g \) can be specified first and should be as large as possible, provided it does not exceed the constraint in Table 10.2.

The next parameter to be selected is \( t_{gap} \), because it needs to be sufficiently short to ensure that the system being measured stays constant. It was decided to set \( t_{gap} \) to 100 \( \mu \)s. \( t_{gap} \) effectively represents the frequency of the bipolar pulse, although only a single positive/negative pulse is produced, not a repeated pulse. In normal circumstances this frequency must be at least double the frequency of the data to be sampled. However, this does not apply here because the FFT is being used to extract signals of a range of frequencies to calculate the impedance.

\( t_{gap} \) dictates \( C_g \), because if \( t_{gap} \) is reduced then a lower value of \( C_g \) is required to produce the same decay prior to the end of the first pulse. Now that \( t_{gap} \) is fixed, we can calculate \( C_g \) required for \( V_T \) to decay to a certain proportion of \( V_g \). It was decided to ensure that \( V_T \) decayed to less than 1% of \( V_g \) prior to the end of the first pulse.

The voltage for current flowing through a single capacitor \( C \) and resistor \( R \) was previously described in Equation (9.8). The circuit shown in Figure 10.10 is more complex and we need to simplify Equation (10.2) for the voltage due to a single capacitor pulse in order to calculate \( C_g \). The derivation of Equation (10.5) is shown in Appendix C.

\[
\therefore V_T \equiv V_g \left[ e^{-\frac{t}{R_g C_g}} + \frac{C_g}{C_{dl}} \left( e^{-\frac{t}{R_g C_{dl}}} \right) \right]
\]  

(10.5)
This is analogous to Equation (9.8).

We want to use Equation (10.5) to calculate the \( C_g \) required to get \( V_T \) to decay to 1\% of \( V_g \) at the end of the first pulse, i.e. at \( t = t_{\text{gap}} \).

\[
0.01V_g \cong V_g \left[ e^{-\frac{t_{\text{gap}}}{R_g C_g}} + \left( \frac{C_g}{C_{\text{dl}}} \right) e^{-\frac{t_{\text{gap}}}{R_{\text{ct}} C_g}} \right]
\]

\[
\therefore e^{-\frac{t_{\text{gap}}}{R_g C_g}} + \left( \frac{C_g}{C_{\text{dl}}} \right) e^{-\frac{t_{\text{gap}}}{R_{\text{ct}} C_g}} - 0.01 \cong 0 \quad (10.6)
\]

Equation (10.6) cannot be solved algebraically because \( C_g \) is in both a linear and exponential term. However, Newton’s method can be used to solve it numerically (Abramowitz and Stegun 1972: 18). This involves making an initial estimate \( C_{g0} \) for the value of \( C_g \), and then a better approximation \( C_{g1} \) is:

\[
C_{g1} = C_{g0} - \frac{f(C_{g0})}{f'(C_{g0})}
\]

Where, from Equation (10.6):

\[
f(C_g) = e^{-\frac{t_{\text{gap}}}{R_g C_g}} + \left( \frac{C_g}{C_{\text{dl}}} \right) e^{-\frac{t_{\text{gap}}}{R_{\text{ct}} C_g}} - 0.01
\]

\[
f'(C_g) = \left( \frac{1}{R_{\Omega} C_g} \right) e^{-\frac{t_{\text{gap}}}{R_g C_g}} + \left( \frac{1}{C_{\text{dl}}} \right) e^{-\frac{t_{\text{gap}}}{R_{\text{ct}} C_g}}
\]

This gives \( C_g = 0.03 \, \text{F} \), for \( R_{\Omega} = 0.3 \, \text{m\Omega} \), \( R_{\text{ct}} = 0.01 \, \Omega \), \( C_{\text{dl}} = 3 \, \text{F} \), \( t_{\text{gap}} = 100 \, \mu\text{s} \).

The final two parameters to be determined are \( f_s \) and \( n \). In addition to the constraints listed in Table 10.2, there needs to be a sufficient number of data points within the time period to allow the FFT to be calculated. It could be considered that 100 data points are required during the first pulse.
\[
\therefore f_s = \frac{100}{t_{gap}} = \frac{100}{100 \times 10^{-6}} = 1 \text{ MHz}
\]

The time over which data is collected must be \( > 2t_{gap} \), to ensure data is collected from both the positive pulse and negative pulse. We have just defined that 100 points will be collected during the first pulse.

\[
\therefore n > 2 \times 100
\]

\[
\therefore n = 256, 512, 1024\ldots
\]

Note that \( f_s/n \) is also a constraint because it is the minimum frequency obtained from the FFT transformation.

Thus the theoretical optimum measurement parameters for determining the series resistance using a bipolar capacitor pulse when \( R_\Omega = 0.3 \text{ m}\Omega, R_{ct} = 0.01 \text{ } \Omega, C_{dl} = 3 \text{ F} \) are summarised in Table 10.4. The calculated current \( I_T \) and voltage \( V_T \) for these values are shown in Figure 10.14, the Nyquist plot is shown in Figure 10.15, and the capacitance plot is shown in Figure 10.16. The fact that (1) the series resistance can be determined as 0.3 m\( \Omega \) from the Nyquist plot, and (2) the capacitance plot is linear with a slope (0.32) very close to the value of \( 1/C_{dl} \) (3 F), suggests that, with appropriate measurement parameters, the series resistance can be measured using a bipolar capacitor pulse. The next step is to build a physical circuit to test the above measurement parameters in the laboratory.

Table 10.4: Optimum measurement parameters for determining series resistance using a bipolar capacitor pulse when \( R_\Omega = 0.3 \text{ m}\Omega, R_{ct} = 0.01 \text{ } \Omega, C_{dl} = 3 \text{ F} \).

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<td>( V_g )</td>
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<tr>
<td>( t_{gap} )</td>
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</tr>
<tr>
<td>( C_g )</td>
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Figure 10.14: Calculated current $I_T$ and voltage $V_T$ for $R_\Omega = 0.3 \text{ m}\Omega$, $R_{ct} = 0.01 \text{ } \Omega$, $C_{dl} = 3 \text{ F}$, $C_g = 0.03 \text{ F}$, $V_g = 100 \text{ V}$, $f_s = 1 \text{ MHz}$, $n = 256$, $t_{gap} = 0.1 \text{ ms}$.

Figure 10.15: Calculated Nyquist plot for $R_\Omega = 0.3 \text{ m}\Omega$, $R_{ct} = 0.01 \text{ } \Omega$, $C_{dl} = 3 \text{ F}$, $C_g = 0.03 \text{ F}$, $V_g = 100 \text{ V}$, $f_s = 1 \text{ MHz}$, $n = 256$, $t_{gap} = 0.1 \text{ ms}$.
Figure 10.16: Calculated capacitance plot for bipolar pulse ($R_\Omega = 0.3 \, \text{m}\Omega$, $R_{ct} = 0.01 \, \Omega$, $C_{dl} = 3 \, \text{F}$, $C_g = 0.03 \, \text{F}$, $V_g = 100 \, \text{V}$, $f_s = 1 \, \text{MHz}$, $n = 256$, $t_{gap} = 0.1 \, \text{ms}$).

### 10.9 Bipolar Capacitor Pulse – Physical Circuit

#### 10.9.1 Experimental

The smelter parameters and optimum measurement parameters determined in the previous chapter are shown in Table 10.5. Some of these values are difficult to achieve in the laboratory, particularly the very low value of 0.3 m\(\Omega\) for $R_\Omega$ and the relatively high value of 3 F for $C_{dl}$. It was calculated that increasing the resistances by a factor of 10 and decreasing the capacitances by a factor of 10 would produce a current $I_T$ and voltage $V_T$ of the same shape, as shown in Figure 10.17. The shape is identical to Figure 10.14, although the current axis scale is lower by a factor of 10. The selected values are also shown in Table 10.5.

The aim was to construct a circuit of as close to the selected parameters as possible. The use of physical components to simulate an electrochemical cell introduces other complications. In an electrochemical cell, $C_{dl}$ is the double layer capacitance and has no resistive component. However, a physical capacitor used to simulate the double layer capacitance will have an equivalent series resistance $R_{dl}$. Therefore, although the desired
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The equivalent circuit to be used in the laboratory is as shown in Figure 10.18a, the actual circuit is shown in Figure 10.18b.

Table 10.5: Optimum and selected parameters for simulation of part of aluminium reduction cell in laboratory.

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<td>3</td>
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</tr>
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</table>

Figure 10.17: Calculated current $I_T$ and voltage $V_T$ for $R_\Omega = 3$ m$\Omega$, $R_{ct} = 0.1$ $\Omega$, $C_{dl} = 0.3$ F, $C_g = 3$ mF, $V_g = 10$ V, $f_s = 1$ MHz, $n = 256$. 
The low values of $R_Ω$ and $R_{ct}$ meant that it was important that the capacitor $C_{dl}$ had a very low $R_{dl}$. A 0.47 F capacitor (Farnell, B-41456-B5470-M) with a typical equivalent series resistance of 3 mΩ (maximum 6 mΩ) was used to represent $C_{dl}$ and $R_{dl}$. Two 1.5 mF capacitors (Vishay, ST 2222-106-19152) were used to represent $C_g$. $R_{ct}$ was constructed from 14.5 mm of 2.1 Ω.ft$^{-1}$ high resistance wire (= 0.10 Ω). $R_Ω$ was initially constructed from 58 strands of 80 mm length, 0.1 mm diameter copper wire (conductivity $58 \times 10^6$ S.m$^{-1}$) (= 3 mΩ). Different values of $R_Ω$ (4.0, 5.0, 6.0 mΩ) were obtained by using longer strands (107 mm, 133 mm, 159 mm respectively). $V_g$ was limited to 10 V to prevent damage to the switches.

The final circuit is shown in Figure 10.19 and a photograph is shown in Figure 10.20. The parameters are summarised in Table 10.6.

The current $I_T$ and voltage $V_T$ were again measured using the LEM PR50 Universal 50 MHz Current Probe and LeCroy Waverunner LT342 digital oscilloscope respectively. As currents up to thousands of Amperes were possible and the Current Probe could measure a maximum of 50 A, two strands were separated from the remaining 58, and the
current was measured just through these two strands. The measured current was multiplied by 58/2 to give the actual current.

Figure 10.19: Equivalent circuit to be used to simulate part of aluminium reduction cell.

Figure 10.20: System to simulate part of aluminium reduction cell in laboratory. Total width of image is 20 cm.
Table 10.6: Optimum, selected and actual parameters for simulation of part of aluminium reduction cell in laboratory.

<table>
<thead>
<tr>
<th>Parameter Type</th>
<th>Parameter</th>
<th>Units</th>
<th>Optimum</th>
<th>Selected</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelter</td>
<td>$R_\Omega$</td>
<td>mΩ</td>
<td>0.3</td>
<td>3</td>
<td>3.0*</td>
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<tr>
<td></td>
<td>$R_t$</td>
<td>Ω</td>
<td>0.01</td>
<td>0.1</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>$C_{dl}$</td>
<td>F</td>
<td>3</td>
<td>0.3</td>
<td>0.47</td>
</tr>
<tr>
<td>Measurement</td>
<td>$C_g$</td>
<td>mF</td>
<td>30</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>$V_g$</td>
<td>V</td>
<td>100</td>
<td>100</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>$f_s$</td>
<td>MHz</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>-</td>
<td>256</td>
<td>256</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>$t_{gap}$</td>
<td>ms</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>$R_{dl}$</td>
<td>mΩ</td>
<td>0</td>
<td>0</td>
<td>3-6</td>
</tr>
</tbody>
</table>

*Values of 4.0, 5.0 and 6.0 mΩ also used

Because of the presence of $R_{dl}$, there is not a true short circuit through the capacitor $C_{dl}$. Therefore the true series resistance $R_T$ is:

$$R_T = R_\Omega + \frac{1}{\frac{1}{R_t} + \frac{1}{R_{dl}}} \quad (10.7)$$

The expected series resistance calculated using Equation (10.7) for each value of $R_\Omega$ is shown in Table 10.7. The expected maximum current is the quotient of $V_g$ and the expected series resistance. The expected maximum voltage is simply $V_g$, because the voltage across the entire circuit is being measured.

Table 10.7: Expected series resistance, maximum current and maximum voltage for simulation of part of aluminium reduction cell in laboratory.

<table>
<thead>
<tr>
<th>$R_\Omega$ (mΩ)</th>
<th>$V_g$ (V)</th>
<th>$R_t$ (Ω)</th>
<th>$R_{dl}$ (mΩ)*</th>
<th>Expected Series Resistance $R_T$ (mΩ)</th>
<th>Expected Max Current $I_T$ (A)</th>
<th>Expected Max Voltage $V_T$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>10</td>
<td>0.10</td>
<td>3</td>
<td>5.9</td>
<td>1700</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>8.7</td>
<td>1200</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.10</td>
<td>3</td>
<td>6.9</td>
<td>1400</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>9.7</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.10</td>
<td>3</td>
<td>7.9</td>
<td>1300</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>11</td>
<td>900</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0.10</td>
<td>3</td>
<td>8.9</td>
<td>1100</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>12</td>
<td>900</td>
<td>10</td>
</tr>
</tbody>
</table>

*R_{dl} is specified to be 3 mΩ typical, 6 mΩ max, so these two values are shown
10.9.2 Derivation of Equations

The presence of $R_{dl}$ changes the equations calculated for a bipolar capacitor pulse in Chapter 10.7, so new equations need to be derived. The derivation of Equation (10.8) for $I_T$ and Equation (10.9) for $V_T$ is shown in Appendix D.

$$I_T = Ae^{kt} \left( k_1 + \frac{k_1 R_{dl}}{R_{ct}} + \frac{1}{R_{ct} C_{dl}} \right) + Be^{kt} \left( k_2 + \frac{k_2 R_{dl}}{R_{ct}} + \frac{1}{R_{ct} C_{dl}} \right) \quad (10.8)$$

$$V_T = Ae^{kt} \left( k_1 R_{ct} + \frac{k_1 R_{dl} (R_{ct} + R_{ct})}{R_{ct}} + \frac{R_{ct} + R_{ct}}{R_{ct} C_{dl}} \right)$$

$$+ Be^{kt} \left( k_2 R_{ct} + \frac{k_2 R_{dl} (R_{ct} + R_{ct})}{R_{ct}} + \frac{R_{ct} + R_{ct}}{R_{ct} C_{dl}} \right) \quad (10.9)$$

It is now possible to determine the current $I_T$ and voltage $V_T$ based on the values of $R_\Omega$, $R_{ct}$, $C_{dl}$, $C_g$, $V_g$, and $R_{dl}$.

10.9.3 Simulation Results

The calculated current $I_T$ and voltage $V_T$ for the ‘Actual’ values from Table 10.6 are shown in Figure 10.21a ($R_{dl}$ was set as 3 m$\Omega$ for the purposes of these calculations). This data was transformed using FFT, and the Nyquist plot is shown in Figure 10.21b. The series resistance as obtained from this figure is 5.9 m$\Omega$, which is the expected value from Table 10.7.
Figure 10.21: Calculations for ‘Actual’ values from Table 10.6 ($R_\Omega = 3 \, \text{m}\Omega$, $R_{ct} = 0.1 \, \Omega$, $C_{dl} = 0.47 \, \text{F}$, $C_g = 1.5 \, \text{mF}$, $V_g = 10 \, \text{V}$, $f_s = 1 \, \text{MHz}$, $n = 256$, $t_{gap} = 0.1 \, \text{ms}$, $R_{dl} = 3 \, \text{m}\Omega$).
10.9.4 Measurement Results

The measured current $I_T$ and voltage $V_T$ for the circuit shown in Figure 10.19 are shown in Figure 10.22a. The shape is very similar to that calculated in Figure 10.21a, but the peak values of current and voltage are about 60% lower than predicted (Table 10.7). This is unsurprising, because the circuitry constructed to deliver the bipolar capacitor pulse will have some external resistance, which would reduce the amount of current that is actually injected into the circuit from the capacitors.

The Nyquist plot is shown in Figure 10.22b: it is totally unlike Figure 10.21b and the ideal Nyquist plot for a Randles equivalent circuit (Figure 4.4), in that (1) the data is highly scattered, and (2) in most cases $-Z'' < 0$.

The scattered data is addressed first. The FFT of the current and voltage are shown in Figure 10.23. The impedances shown in Figure 10.22b are calculated from the quotient of the voltages and currents shown in Figure 10.23. Any quotient calculation where one or both values are close to zero is subject to large error. These are indicated by arrows in the figures, and would also include most data above 100 kHz.

Figure 10.22b is reproduced in Figure 10.24, except that data is indicated as ‘included’ or ‘excluded’ on the basis of the magnitude of the voltage at each frequency. Data has been excluded if the magnitude of the voltage is less than 0.05 V, a somewhat arbitrary figure. The included data now exhibits a linear trend.

The second observation, that $-Z'' < 0$ for all the data, can be explained by inductance. The specification for the 0.47 F capacitor was that it had a self-inductance $L_{sl}$ of ~20 nH. This means that a better representation of the circuit is as shown in Figure 10.25. The Zview computer program (Johnson 2000) was used to calculate the theoretical Nyquist plot if EIS of frequencies 4-70 kHz was applied to the circuit shown in Figure 10.25, and the result is shown in Figure 10.26. This is closer to the measured result in Figure 10.24.
Figure 10.22: Measurements for circuit shown in Figure 10.19 ($R_\Omega = 3.0$ m$\Omega$, $R_{ct} = 0.10$ $\Omega$, $C_d = 0.47$ F, $C_g = 1.5$ mF, $V_g = 10.0$ V, $f_s = 1$ MHz, $n = 256$, $t_{gap} = 0.1$ ms, $R_{dl} \approx 3$ m$\Omega$).
Figure 10.23: FFT transforms of current $I_T$ and voltage $V_T$ for circuit shown in Figure 10.19 ($R_\Omega = 3.0 \text{ m}\Omega$, $R_{cl} = 0.10 \ \Omega$, $C_{dl} = 0.47 \ \text{F}$, $C_g = 1.5 \ \text{mF}$, $V_g = 10.0 \ \text{V}$, $f_s = 1 \ \text{MHz}$, $n = 256$, $t_{gap} = 0.1 \ \text{ms}$, $R_{dl} \approx 3 \ \text{m}\Omega$). Arrows indicate the type of data where large error can result during calculation of impedance.

Figure 10.24: Reproduction of Figure 10.22b; ‘included’ data is where the magnitude of the voltage transform is $> 0.05 \ \text{V}$. 
Figure 10.25: Equivalent circuit to be used to simulate part of aluminium reduction cell, including inductance.

Figure 10.26: Nyquist plot if EIS of frequencies 4-70 kHz was applied to the circuit shown in Figure 10.25.
Although inductance is present, the series resistance can still be determined if the data intersects the $-Z'' = 0$ axis. Examining the included data more closely in Figure 10.27, the data closest to $-Z'' = 0$ is the lowest frequency of the FFT transform, in this case 4 kHz. It is likely that data at an even lower frequency may be at $-Z'' > 0$, i.e. the data would intersect the $-Z'' = 0$ axis. A way of obtaining data at a lower frequency is to increase $n$, as the lowest frequency obtained from the FFT is $f_s/n$. The measured current $I_T$ and voltage $V_T$ for $n = 1024$ is shown in Figure 10.28a and the Nyquist plot is shown in Figure 10.28b (note: in this case the threshold for including data on the Nyquist plot was that the magnitude of the voltage had to be $> 0.04$ V, rather than $> 0.05$ V as previously). From interpolation, $Z' = 5.1 \text{ m}\Omega$ at $-Z'' = 0$. Thus it could be concluded that the series resistance is 5.1 mΩ.

Figure 10.27: Reproduction of Figure 10.24, showing included data only.
Figure 10.28: Measurements for circuit shown in Figure 10.19 ($R_Ω = 3.0 \, \text{mΩ}$, $R_{cl} = 0.10 \, \Omega$, $C_{dl} = 0.47 \, \text{F}$, $C_g = 1.5 \, \text{mF}$, $V_g = 10.0 \, \text{V}$, $f_s = 1 \, \text{MHz}$, $n = 1024$, $t_{gap} = 0.1 \, \text{ms}$, $R_{dl} \approx 3 \, \text{mΩ}$).
As mentioned previously, different values of $R_\Omega$ (4.0, 5.0, 6.0 mΩ) were obtained by using longer strands of wire in the circuit. The Nyquist plots for $R_\Omega = 3$ mΩ (1 measurement), 4 mΩ (1), 5 mΩ (4) and 6 mΩ (5) are shown in Figure 10.29 and summarised in Table 10.8. Overall, a 1 mΩ increase in $R_\Omega$ results in a ~1 mΩ increase in the series resistance, although the data for $R_\Omega = 5$ mΩ does not match the trend. This was the last data collected so perhaps some experimental error had been introduced. An obvious source of error would be an incorrect length of wire, but this was checked.

As stated in Chapter 10.9.3, the series resistance is not expected to be equal to $R_\Omega$, because of the presence of $R_{dl}$. The results presented here suggest that $R_{dl} = 2$ mΩ, not dissimilar to the specified typical value of 3 mΩ.

As a broad approximation, the maximum voltage measured was ~5 V over the range of tests; half the value of $V_g$. This suggests that the external resistance was of a similar magnitude to the series resistance, i.e. ~7 mΩ.

Figure 10.29: Nyquist plots for circuit shown in Figure 10.19 ($R_{cl} = 0.10$ Ω, $C_{dl} = 0.47$ F, $C_g = 1.5$ mF, $V_g = 10.0$ V, $f_s = 1$ MHz, $n = 1024$, $t_{gap} = 0.1$ ms, $R_{dl} \approx 3$ mΩ).
Table 10.8: Summary of series resistances obtained from Nyquist plots in Figure 10.29.

<table>
<thead>
<tr>
<th>$R_\Omega$ (Ω)</th>
<th>Measurement #</th>
<th>Date</th>
<th>Max Current (A)</th>
<th>Max Voltage (V)</th>
<th>Series resistance determined from Nyquist plot (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>24 July 2009</td>
<td>470</td>
<td>4.1</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>15 April 2011</td>
<td>500</td>
<td>4.1</td>
<td>5.9</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>29 April 2011</td>
<td>470</td>
<td>3.8</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td>460</td>
<td>3.8</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>480</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td>480</td>
<td>5.0</td>
<td>6.2</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>20 April 2011</td>
<td>430</td>
<td>4.5</td>
<td>7.9</td>
</tr>
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<td>7.8</td>
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<td>3</td>
<td></td>
<td>420</td>
<td>5.6</td>
<td>7.7</td>
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<td>5</td>
<td></td>
<td>420</td>
<td>4.4</td>
<td>7.7</td>
</tr>
</tbody>
</table>

It is also worth highlighting that the frequency at which the data intersected the $-Z’ = 0$ axis was generally ~2 kHz. This is far lower than the 30-70 kHz reported for the EIS measurements on the KOH system in Chapter 9.2.3. This can be explained as follows.

Rearranging Equation (4.6):

$$\omega^2 Z'' C_{dl}^2 R_{ct}^2 - \omega C_{dl} R_{ct}^2 + Z'' = 0$$

$$\therefore \omega = \frac{C_{dl} R_{ct}^2 \pm \sqrt{(C_{dl} R_{ct}^2)^2 - 4Z''^2 C_{dl}^2 R_{ct}^2}}{2Z'' C_{dl} R_{ct}^2}$$

$$\therefore \omega = \frac{1}{2Z'' C_{dl}} \pm \frac{\sqrt{4Z''^2 C_{dl}^2 R_{ct}^2 - R_{ct}^2}}{2Z'' C_{dl} R_{ct}^2}$$

$$\therefore \omega = \frac{1}{2Z'' C_{dl}} \pm \frac{1}{C_{dl} R_{ct}} \sqrt{R_{ct}^2 - 4Z''^2}$$

$$\therefore \omega = \frac{1}{2Z'' C_{dl}} \pm \frac{1}{R_{ct} C_{dl}} \sqrt{R_{ct}^2 - 4Z''^2}$$

(10.10)

We want to find $\omega$ at which $Z’$ tends to zero. If we let $Z'' = 1$ mΩ then, for the values of $R_{ct}$ and $C_{dl}$ shown in Table 10.6, $\omega = 3$ Hz and 330 Hz, i.e. $Z’ < 1$ mΩ for $\omega < 3$ Hz and $> 295$ Hz. Thus a frequency of 295 Hz should be sufficient to determine the series resistance from a Nyquist plot. The reason that this is far lower than the 30-70 kHz
reported for the EIS measurements on the KOH system is that the capacitance $C_{dl}$ is very large in this physical circuit (designed to represent an industrial aluminium reduction cell) compared to a typical laboratory-scale electrolysis cell. This analysis excludes inductance but the results can be considered illustrative.

10.10 Conclusions

The likely values of $R_{\Omega}$, $R_{ct}$ and $C_{dl}$ in industrial cells have been established and equations for the total current $I_T$ and voltage $V_T$ have been derived. Based on these equations, it was found that $V_T$ does not decay to zero for a single positive pulse from the discharge of a capacitor, and this appears to mean that a Nyquist plot cannot be used to determine the series resistance.

The equations were modified to represent a bipolar pulse, i.e. a positive pulse produced by a capacitor charged to $V_g$, followed by a negative pulse produced by a capacitor charged to $-V_g$. This resulted in the final value of $V_T$ being much closer to zero. This appears to allow the series resistance to be determined from a Nyquist plot.

In combination with the likely values of $R_{\Omega}$, $R_{ct}$ and $C_{dl}$ in industrial cells, the equations for $I_T$ and voltage $V_T$ have were simplified to allow the measurement parameters ($C_g$, $V_g$, $f_s$, $n$, $t_{gap}$) to be selected.

A physical circuit was constructed to represent the values of $R_{\Omega}$, $R_{ct}$ and $C_{dl}$, except that the resistances and capacitances had to be scaled by a factor of 10. The equations had to be modified to account for the equivalent series resistance in the capacitor. The Nyquist plots of the measured data were significantly different to the predictions, but this could largely be accounted for by inductance. The series resistance could be determined with slight modifications to the measurement parameters.

The next step is to investigate whether the series resistance can be obtained on an electrolytic cell of similar geometry to an industrial aluminium reduction cell.
CHAPTER 11 – CURRENT INJECTION USING A CAPACITOR – VALIDATION ON COPPER ELECTROWINNING CELL

11.1 Introduction

The determination of the series resistance of a physical circuit designed to represent an industrial aluminium reduction cell was described in Chapter 10. A number of aspects would be different in measurements on an industrial cell:

1. It is a real electrolytic cell, not a physical representation;
2. Geometry may be a factor, as the anode dimensions are in the order of 1 m;
3. The magnitude of the inductance is unknown and may be significant;
4. There is a significant magnetic field present;
5. Experimentation would be difficult, due to high temperatures, corrosive environment and interaction with cell operations.

Therefore it was considered prudent to first investigate whether the bipolar capacitor technique is viable on a real electrolytic cell of dimensions similar to that of an industrial aluminium reduction cell, without interference from items 4 and 5 from the above list.

It would be expensive to construct an electrolytic cell of the required dimensions specifically for this task. However, a full-scale, transparent copper electrowinning cell was available. Coincidentally, the dimensions of the anodes and cathodes in this cell were not dissimilar to an industrial aluminium reduction cell

Measurements on this copper electrowinning cell are described in this chapter. This was also a good opportunity to test aspects that would be required for measurements on an industrial aluminium reduction cell so, for example, some new equipment more suitable for industrial measurements was used.
11.2 Experimental

11.2.1 Cell Specification

The Perspex copper electrowinning cell is shown in Figure 11.1. The overall electrochemical reactions are:

\[
\begin{align*}
\text{Anode:} & \quad \text{O}_2(g) + 4\text{H}^+_{(aq)} + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}(l) & E^0 = +1.23 \text{ V} \quad (11.1) \\
\text{Cathode:} & \quad \text{Cu}^{2+}_{(aq)} + 2\text{e}^- = \text{Cu(s)} & E^{2\circ} = +0.34 \text{ V} \quad (11.2)
\end{align*}
\]

And the overall cell reaction is:

\[
2\text{CuSO}_4_{(aq)} + 2\text{H}_2\text{O}(l) \leftrightarrow 2\text{Cu(s)} + \text{O}_2(g) + 4\text{HSO}_4_{(aq)} & \quad E = -0.89 \text{ V} \quad (11.3)
\]

The specifications of the cell are shown in Table 11.1. The reason for using this cell is that many aspects are similar to the Point Henry aluminium reduction cell (Table 11.2). In particular, the resistance in the ACG is very similar. The maximum resistance in the ACG is 2.3 mΩ (Equation (3.2)) if one anode is used with an 80 mm ACD. However, there are also a number of differences (Table 11.3). This means that the results cannot be directly applied to an aluminium reduction cell.

Table 11.1: Specifications of laboratory copper electrowinning cell

<table>
<thead>
<tr>
<th>Component</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodes</td>
<td>Material</td>
<td>Lead</td>
</tr>
<tr>
<td></td>
<td>Number</td>
<td>Two (either side of cathode)</td>
</tr>
<tr>
<td></td>
<td>Area</td>
<td>0.5 m² each, 1.0 m² total</td>
</tr>
<tr>
<td>Cathode</td>
<td>Material</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>H₂SO₄ Concentration</td>
<td>200 g/L (2.0 M)</td>
</tr>
<tr>
<td></td>
<td>CuSO₄ Concentration</td>
<td>40 g/L (0.25 M)</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td></td>
<td>Elec. Conductivity</td>
<td>0.7 S.cm⁻¹ (from Figure 11.2)</td>
</tr>
<tr>
<td>Cell</td>
<td>Current</td>
<td>500 A max</td>
</tr>
<tr>
<td></td>
<td>Current Density</td>
<td>0.10 A.cm⁻² max (500 A with one anode used)</td>
</tr>
<tr>
<td></td>
<td>ACD</td>
<td>40-80 mm. Initial configuration 56 mm.</td>
</tr>
</tbody>
</table>
Figure 11.1: Laboratory copper electrowinning cell.
Figure 11.2: Electrical conductivity of 200 g/L H_2SO_4-CuSO_4-H_2O (Tozawa et al. 2003).

Table 11.2: Important similarities between laboratory copper electrowinning cell and Point Henry aluminium reduction cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Laboratory Copper Electrowinning Cell</th>
<th>Point Henry Aluminium Reduction Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte Conductivity</td>
<td>0.7 S.cm⁻¹</td>
<td>2.1 S.cm⁻¹</td>
</tr>
<tr>
<td>Anode Area</td>
<td>0.5, 1.0 m²</td>
<td>0.84 m²</td>
</tr>
<tr>
<td>Resistance in ACD</td>
<td>1.1-2.3 mΩ</td>
<td>0.3 mΩ</td>
</tr>
</tbody>
</table>

Table 11.3: Important differences between laboratory copper electrowinning cell and Point Henry aluminium reduction cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Laboratory Copper Electrowinning Cell</th>
<th>Point Henry Aluminium Reduction Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation</td>
<td>Vertical</td>
<td>Horizontal</td>
</tr>
<tr>
<td>Current Density</td>
<td>0.05 A/cm²</td>
<td>0.9 A/cm²</td>
</tr>
<tr>
<td>Gas Bubbles</td>
<td>Small O_2</td>
<td>Large CO_2</td>
</tr>
<tr>
<td>Metal deposition</td>
<td>Solid Cu onto stainless steel</td>
<td>Molten Al onto molten Al</td>
</tr>
</tbody>
</table>
11.2.2 Cell Parameters

The likely values of $C_{dl}$, $R_\Omega$ and $R_{ct}$ in the copper electrowinning cell have to be estimated, as was done for the aluminium reduction cell in Chapter 10.2. From Table 11.2, $R_\Omega = 1.1-2.3 \text{ m}\Omega$, and more specifically 1.6 m$\Omega$ for 56 mm ACD (the initial configuration).

Copper electrowinning was studied in two laboratory configurations to investigate some of the parameters (Muresan et al. 1999). The first consisted of a brass sheet cathode with two parallel lead plate anodes. The total cathode area was 2.25 cm$^2$. The charge transfer resistance $R_{ct}$ was found to be ~0.10 $\Omega$ from measurements on this cell. The second configuration had a copper disk electrode. The double layer capacitance $C_{dl}$ was found to be ~160 $\mu$F/cm$^2$ from measurements on this cell. Thus the capacitance would be 0.8 F for an anode area of 0.5 m$^2$.

11.2.3 Measurement Parameters

It was described in Chapter 10.8 that the five measurement parameters should be determined in the order $V_g$, $t_{gap}$, $C_g$, $f_s$, $n$.

Recall that it is preferable to maximise $V_g$ to maximise the signal. The switches used in the measurements on the Randles equivalent circuit (Chapter 10.9.1) were modified so that they could handle 100 V, instead of the previous limit of 10 V. However, some preliminary experiments conducted at 100 V damaged the switches. Therefore all experiments reported here were conducted with $V_g = 30$ V.

$t_{gap}$ was set at 100 $\mu$s as per the previous measurements on the Randles equivalent circuit.

The desired value of $C_g$ was calculated to be 16 mF using Newton’s method, as previously described in Chapter 10.8. The nearest easily-obtainable capacitor was 10 mF, so this was used.

The LeCroy Waverunner LT342 digital oscilloscope used in the experiments reported in previous chapters would not be suitable for measurements on an industrial aluminium
reduction cell, because it could not be connected to a personal computer and data could only be extracted using a 3.5” floppy disk drive. Therefore a different oscilloscope was used for these tests; a Pico Technology PicoScope 6402 (DC accuracy ±3%). It was desired to have the same $f_s$ and $n$ as per the measurements on the Randles equivalent circuit; 1 MHz and 1024 respectively. However, the data acquisition frequency is not directly specified in the PicoScope, rather it is a function of the µs/div and the number of data points acquired. Therefore $f_s$ was actually 820 kHz.

All the cell and measurement parameters discussed above are summarised in Table 11.4.

Table 11.4: Values evaluated using equations for $I_T$ and $V_T$ for copper electrowinning cell

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\Omega}$</td>
<td>mΩ</td>
<td>1.6</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Ω</td>
<td>0.10</td>
</tr>
<tr>
<td>$C_{dl}$</td>
<td>F</td>
<td>0.8</td>
</tr>
<tr>
<td>$C_g$</td>
<td>mF</td>
<td>10</td>
</tr>
<tr>
<td>$V_g$</td>
<td>V</td>
<td>30</td>
</tr>
<tr>
<td>$f_s$</td>
<td>kHz</td>
<td>820</td>
</tr>
<tr>
<td>$n$</td>
<td>-</td>
<td>1024</td>
</tr>
<tr>
<td>$t_{gap}$</td>
<td>ms</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Recall that the LEM PR50 Universal 50 MHz Current Probe used to measure the current on the Randles equivalent circuit can measure a maximum of 50 A, and that the current was measured on a small percentage of the strands to stay within this limit. The current through the anode on an industrial aluminium reduction cell would be many orders of magnitude higher, and it would be difficult to attach a separate, small conductor to the anode rod to allow the measured current to be less than 50 A. Therefore a CWT150B/4/1000 Rogowski coil (Power Electronic Measurements Ltd, U.K - Figure 11.3) was used, which can measure currents from 15 A to 30 kA, at frequencies up to 10 MHz, at a typically accuracy of ±0.2%. The coil (the red section Figure 11.3) is 1000 mm long, making it suitable for measurements on an anode rod. This coil was used to measure the current on the copper electrowinning cell.
11.2.4 Experimental Conditions

Preliminary experiments were conducted with two anodes. The advantage of using one anode is that higher current densities were possible, which would produce more bubbles and hence the resistance due to bubbles should be easier to detect. All the experiments reported here are with one anode.

For the initial experiments with one anode the ACD was 56 mm. Subsequently the cell was reconfigured to allow a larger range of ACDs, and three were used; 40, 60 and 80 mm. Measurements were conducted at 0, 200 and 400 A, equivalent to current densities of 0, 0.04 and 0.08 A.cm\(^{-2}\) respectively. This gives a total of nine combinations, and 10 measurements were made for each combination.

Note that only \(~25\%\) of the gas volume is produced for a given current density in the copper electrowinning cell compared to an aluminium reduction cell. This is because the temperature of the copper electrowinning cell is much lower.
11.3 Results

11.3.1 Simulation Results

The expected maximum current and voltage can be broadly estimated. If $R_\Omega \approx 1.6 \, \text{m}\Omega$ and the connection resistance is assumed to be the same as that calculated from the earlier experiments on the Randles equivalent circuit ($\approx 7 \, \text{m}\Omega$ - Chapter 10.9), then the total resistance is $\approx 10 \, \text{m}\Omega$. Given $V_g = 30 \, \text{V}$, this would give an expected maximum voltage of $6 \, \text{V}$ and maximum current of $3,500 \, \text{A}$.

Using the values in Table 11.4, except $V_g = 6 \, \text{V}$, and Equations (B7) and (B8), the calculated current $I_T$ and voltage $V_T$ are shown in Figure 11.4a, and the calculated Nyquist plot is shown in Figure 11.4b.

11.3.2 Measurement Results

11.3.2.1 Preliminary

The measured current $I_T$ and voltage $V_T$ for 56 mm ACD, current density $i = 0$ is shown in Figure 11.5a. The voltage is as expected; the maximum is $6 \, \text{V}$ and the pulses decay close to zero. Note that there is a DC offset because it is a live electrochemical cell. The current is very different to that expected; it is slow to increase and only reaches $\approx 10\%$ of the expected maximum of $3,500 \, \text{A}$.

The Nyquist plot is shown in Figure 11.5b. Although it is very different to Figure 11.4b and the data does not intersect the $-Z' = 0$ axis, an extrapolation of the trend suggests that the series resistance is $1.5 \, \text{m}\Omega$; in line with that expected.

The time series data and the Nyquist plot both strongly suggest the presence of inductance. For the former, the impedance must be an order of magnitude larger than expected if the voltage is as expected and the current is an order of magnitude lower than expected. Given that the series resistance was as expected, this additional impedance is likely to be inductance. For the Nyquist plot, the fact that $-Z' < 0$ for all data indicates the presence of inductance.
It would be better if the data could be made to intersect the $-Z' = 0$ axis, and it is apparent from the Nyquist plot that a component wave of frequency less than 800 Hz is required. Note that 800 Hz is the quotient of $f_s$ (820 kHz) and $n$ (1024), so $f_s/n$ needs to be reduced, which requires that either $f_s$ be reduced or $n$ be increased. The issue with increasing $n$ is that the time series is divided into more components, which reduces the magnitude of each component. This increases the error when calculating the impedance as the quotient of the voltage and current, as described in Chapter 10.9.4.

If $f_s$ is reduced, then a number of issues arise. Firstly, reducing $f_s$ may make the entire measurement invalid. Recall that the faradaic impedance $Z_f$ can only be simplified to a charge-transfer resistance $R_{ct}$ at high frequencies (Chapter 4.3.4). If $f_s$ is too low, then the series resistance obtained from the Nyquist plot will not just be $R_Q$; it will include a resistive component from the faradaic impedance.

Secondly, less data will be collected in a given time period. If we want to maintain that 100 points are collected during the first pulse, then $t_{gap}$ has to be increased commensurately with the decrease in $f_s$. This increases the risk that the system will not remain stable during each measurement. If we want to retain constant $t_{gap}$, then less data will be collected in the time period, probably increasing the error in the measurement.

All the above approaches (increasing $n$, reducing $f_s$ and commensurately increasing $t_{gap}$, reducing $f_s$ and keeping $t_{gap}$ constant) were attempted, but none of them produced a Nyquist plot where the data intersected the $-Z' = 0$ axis. It was decided to retain the original parameters (Table 11.4).

The Nyquist plots for the 10 measurements at 40 mm ACD / 0 A.cm$^2$ are shown in Figure 11.6 to illustrate the variation, which is reasonably significant. There appears to be a cluster of similar results (Measurement 1-4, 8, 10) and perhaps the others are outliers, but there is no specific justification to exclude these results. The 10 measurements were made one after the other over a ~5 minute period. The equivalent data for 60 mm and 80 mm ACD are not shown, but exhibited a similar pattern.
Figure 11.4: Calculations for values from Table 11.4 ($R_\Omega = 1.6 \, \text{m\Omega}$, $R_{ct} = 0.1 \, \Omega$, $C_{dl} = 0.8 \, \text{F}$, $C_g = 10 \, \text{mF}$, $V_g = 6 \, \text{V}$, $f_s = 820 \, \text{kHz}$, $n = 1024$, $t_{gap} = 0.1 \, \text{ms}$).
Figure 11.5: Measurements for copper electrowinning cell (ACD = 56 mm, \( i = 0 \) A.m\(^2\), \( C_g = 10 \) mF, \( V_g = 30 \) V, \( f_s = 820 \) kHz, \( n = 1024 \), \( t_{gap} = 0.1 \) ms).
11.3.2.2 Effect of ACD

The Nyquist plots for the 10 measurements at 0 A.cm\(^{-2}\) at each ACD are shown in Figure 11.7. The 10 measurements at each ACD are shown with the same symbol. The series resistance clearly increases with increasing ACD.

In an attempt to calculate the series resistance more accurately, lines of regression were calculated for each of the 30 measurements, using the four lowest frequency data points for each. The x-intercept, i.e. the series resistance, can be directly calculated by extrapolating each line of regression. Examples are shown for Measurement 1 for each ACD in Figure 11.8. From the figure, the series resistances are 1.16 mΩ at 40 mm ACD, 1.46 mΩ at 60 mm ACD and 2.09 mΩ at 80 mm ACD. The standard error of each of the 30 intercepts was typically less than 5% (detailed results shown in Appendix E).

The series resistance for each measurement calculated using this method is shown in Figure 11.9, which highlights the clear effect of ACD. The effect of ACD is statistically significant to the 99% confidence level, as measured by a t-test.
The y-intercept of the regression line in Figure 11.9, $0.28 \text{ m}\Omega$, is the series resistance at zero ACD. This would include the bubble resistance, but probably also resistance in the connections etc.

The slope of the regression line in Figure 11.9, $0.022 \text{ m}\Omega/\text{mm}$, is equal to $1/\kappa A$, so the electrical conductivity $\kappa$ is $0.9 \text{ S.cm}^{-1}$ based on these results. This is higher than the expected value of $0.7 \text{ S.cm}^{-1}$ for $40 \text{ g/L CuSO}_4$ (Figure 11.2). This triggered a recheck of the electrolyte composition, which was measured to be $11.5 \text{ g/L CuSO}_4$ at the conclusion of the measurements, which gives an expected electrical conductivity of $0.8 \text{ S.cm}^{-1}$. The fact that the measurements of series resistance correctly indicated that the electrical conductivity was higher than that expected gives further confidence to the technique.

Figure 11.7: Nyquist plot for 10 measurements at each ACD on copper electrowinning cell ($i = 0 \text{ A.cm}^2$, $C_g = 10 \text{ mF}$, $V_g = 30 \text{ V}$, $f_s = 820 \text{ kHz}$, $n = 1024$, $t_{gap} = 0.1 \text{ ms}$). All measurements at each ACD are depicted with same symbol.
Figure 11.8: Part of Nyquist plot for Measurement 1 at each ACD on copper electrowinning cell, showing intercepts with $-Z'' = 0$ axis of lines of regression $(i = 0 \text{ A}\cdot\text{cm}^{-2}, C_g = 10 \text{ mF}, V_g = 30 \text{ V}, f_s = 820 \text{ kHz}, n = 1024, t_{gap} = 0.1 \text{ ms})$.

Figure 11.9: Series resistance of copper electrowinning cell calculated using lines of regression on Nyquist plot $(i = 0 \text{ A}\cdot\text{cm}^{-2}, C_g = 10 \text{ mF}, V_g = 30 \text{ V}, f_s = 820 \text{ kHz}, n = 1024, t_{gap} = 0.1 \text{ ms})$. 

$y = 0.0223x + 0.28$
11.3.2.3 Effect of Current Density

A more direct way of assessing the effect of bubbles is to examine the effect of current density on the series resistance. The series resistance for each measurement at 40 mm ACD / 0, 0.04, 0.08 A.cm\(^{-2}\) is shown in Figure 11.10: current density has a negligible effect on the series resistance. This suggests that the amount of gas bubbles was insufficient to have an effect on the series resistance.

This can be checked by considering the void fraction of bubbles and the thickness of the bubble layer. In separate work on the same copper electrowinning cell, the void fraction in the bubble layer was measured using a high speed camera and the bubble layer thickness could be directly observed. At 0.02 A.cm\(^2\), the void fraction was \(~4\%\) and the bubble layer was 6 mm thick. Using Equation (3.16), the resistance with such a bubble layer is only expected to be 0.6\% higher than the resistance without the bubble layer, for 40 mm ACD. Therefore it is unsurprising that no increase in series resistance was measured with an increase in current density, because only a \(~1\%\) change would be expected, and this is too small to be detected given the variation in the measurements. It is possible that an effect of current density could be detected if many more measurements were performed.
Figure 11.10: Series resistance of copper electrowinning cell calculated using lines of regression on Nyquist plot (ACD = 40 mm, \( C_g = 10 \) mF, \( V_g = 30 \) V, \( f_s = 820 \) kHz, \( n = 1024 \), \( t_{gap} = 0.1 \) ms).

11.4 Conclusions

The series resistance of the copper electrowinning cell could be determined using the bipolar capacitor technique, even though inductance had a significant effect on the measurements. This is because by definition the series resistance is determined where the imaginary impedance (due to capacitance and/or inductance) is zero. However, inductance had two significant consequences. Firstly, it reduced the current produced by the discharge of the capacitor. This reduced the voltage produced by the passage of that current through the ohmic resistance. Secondly, it affected the frequency at which the imaginary impedance was zero, and in many cases no data could be obtained where the imaginary impedance was zero.

The series resistance increased with increasing ACD, as expected, and the incremental increase in resistance was proportional to the electrical conductivity of the electrolyte.
As the scale of an industrial aluminium reduction cell is similar to the copper electrowinning cell, this gives some confidence that the series resistance of an industrial aluminium reduction cell could be measured using the bipolar capacitor technique.

The next section summarises the work completed in this thesis and makes recommendations for further work.
SECTION D:

CONCLUSIONS AND RECOMMENDATIONS
CHAPTER 12 – CONCLUSIONS

The original objectives of this thesis (Chapter 1.3) are restated below:

1. Measure the bubble behaviour in an industrial aluminium reduction cell;
2. Demonstrate that a physical model can provide a sufficiently accurate representation of bubble behaviour in an industrial aluminium reduction cell, in terms of its effect on electrolyte resistance.

After reviewing the relevant studies (Chapter 8.2), it was decided that the focus would be the effect of gas bubbles on ohmic resistance.

A measurement technique was developed based on the principle of electrochemical impedance spectroscopy. Measurements were conducted on a physical electrical circuit designed to represent an industrial aluminium reduction cell. Inductance had a significant impact on the performance of the measurement technique, but the measurement parameters could be optimised such that the ohmic resistance of the circuit could be determined.

Measurements were conducted on a 500 A laboratory copper electrowinning cell with geometry similar to that of an industrial aluminium reduction cell. Inductance again had a significant impact on the performance of the measurement technique, in that:

1. It reduced the current produced by the discharge of the capacitor;
2. It affected the frequency at which the imaginary impedance was zero.

The implications of these two issues for measurements on industrial aluminium reduction cells are:

1. The voltage produced through the ACG is reduced, which will make it more difficult to detect and quantify this voltage in order to determine the series resistance;
2. It can be difficult to formulate a set of measurement parameters that will allow the series resistance to be determined. There may be configurations where the series resistance cannot be determined.

However, there is no fundamental reason why the bipolar capacitor technique could not be used to measure the series resistance on industrial aluminium reduction cells. Recommendations on how to conduct these measurements are provided in the next chapter.

The above discussion means that only the first objective listed at the start of this chapter was addressed, as the complexity of achieving this had been underestimated.
CHAPTER 13 - RECOMMENDATIONS FOR MEASUREMENTS ON ALUMINIUM REDUCTION CELLS

13.1 Introduction

The preceding sections have demonstrated that it is feasible to use the bipolar capacitor technique to measure the series resistance in an industrial aluminium reduction cell. Unfortunately, measurements were not possible within the timeframe of this study. The purpose of this chapter is to outline the planning for smelter measurements.

13.2 Measurement System

The measurement system would consist of:

- A box containing the two capacitors for injecting charge and the required switching circuitry. The capacitors could be charged by mains power or batteries. Batteries are probably preferred because (1) there are difficulties with using power cables in reduction lines, (2) power cables introduce trip hazards, and (3) the capacitor pulses are of sufficiently low energy that standard batteries would provide sufficient energy for many measurements;
- A Rogowski coil for measuring the current through the anode rod. The coil is rated to 100 °C, so some work may be involved to ensure it stays within this limit;
- A battery-powered oscilloscope to record the current and voltage. This could be programmed to transmit all data to a PC, or automatically perform the FFT and transmit the processed data.

The ability to measure the resistance of the ACD under an anode is dictated by two issues. Firstly, there is the relative proportions of the ACD resistance and the total resistance of the circuit in which the current is injected. The resistance of the ACD under an anode is very low; ~0.3 mΩ, so it would be important to measure the voltage across the ACD and as little else as possible. The most practical measurement may be between the metal pad and a point on the anode rod above the hood, but this will mean that the resistance of the anode, stubs and yoke are included. It would also be imperative to
minimise the connection resistance, i.e. of the switches and of the connection to the anode rod. Any current injected into an anode rod will not only travel down through the selected anode rod, but also up into the anode beam and then down every other anode rod to the metal pad. Somewhat counter-intuitively, this does not reduce the amount of current travelling down the selected anode rod, as it is the total voltage that is constant, not the current, and it is a parallel circuit\(^1\).

Secondly, and perhaps more importantly, inductance is a significant unknown and difficult to predict. It is likely that inductance will limit the amount of current that can be injected, which may prevent the series resistance from being determined. An alternative would be to charge two inductors to inject charge into the anode rod, instead of two capacitors. These inductors would overcome any inductance in the circuit. However, this would probably only exchange one set of problems for another, in that the capacitance of the circuit would limit the voltage.

### 13.3 Experimental Configurations

Assuming it is possible to measure the series resistance for a particular anode, a number of different measurements could be made to provide different information on the process:

1. The series resistance could be measured at different ACDs. At relatively large ACDs, the relationship between series resistance and ACD should be linear (as per Figure 11.9). As the ACD is reduced to approximately the bubble layer thickness, the relationship will become non-linear. This will provide an indication of the bubble layer thickness.

2. The series resistance could be measured on an anode that has been insulated from the anode beam. This would mean that no DC current is flowing through that anode; hence no bubbles would be generated under that anode. The difference between this series resistance and the resistance measured with DC current should be the resistance due to bubbles. Some issues with this measurement are:

\[^1\text{E.g. If a capacitor charged to 100 V is discharged through a 1 m\(\Omega\) anode rod, then 100 kA will be produced. If the current also goes through 20 other anode rods each of 1 m\(\Omega\), then the current through each of these will still be 100 kA.}\]
Chapter 13 - Recommendations for Measurements on Aluminium Reduction Cells

- The anode must be in exactly the same position (i.e. keep the ACD constant), otherwise the change in resistance between the two configurations will not be just due to bubbles. This will be difficult given that the anode will have to be moved to fit an insulator between the rod and beam. Also anode beam movement will probably need to be prevented for the duration of measurement on one configuration;
- The DC current and bubble generation may cause oscillation in the metal pad and hence a change in ACD. Even if the anode is kept in exactly the same position, the ACD may change because of a change in position of the metal pad.

3. The series resistance could be measured on anodes of different ages and slot design to determine the effect of anode condition.
4. The series resistance could be measured at different current densities. The difference between the overall voltage change (also from the anode rod to the metal pad) and the ohmic voltage change would be an indication of the anodic polarisation. It is recognised that altering the current density of a reduction cell is a significant disruption to operations.

The results in this study show that there is significant variation in the measurements for a given configuration. This can be overcome by performing a large number of measurements. Fortunately, each measurement is practically instantaneous, so the system could be programmed to automatically perform, say, 100 measurements over several minutes. The main factor is the amount of time needed to recharge the capacitors between each measurement: in this study it was about five seconds.

In summary, the results from this study demonstrate that it should be possible to measure the electrical resistance on industrial aluminium reduction cells and determine if this is significantly affected by anode design and condition. If this can be achieved, then it is likely that this information can be used to improve cell performance.
APPENDIX A

Derivation of equations for single capacitor pulse through Randles equivalent circuit

For these equations, let $t = 0$ be the time at which the capacitor commences discharging.

1. Voltages are equal in parallel:

   $\therefore V_{ct} = V_{dl}$

   $\therefore I_{ct} R_{ct} = \frac{q_{dl}}{C_{dl}}$

   $\therefore \frac{dq_{ct}}{dt} R_{ct} = \frac{q_{dl}}{C_{dl}}$

   $\therefore q_{dl} = C_{dl} \frac{dq_{ct}}{dt}$

   $\therefore \frac{dq_{dl}}{dt} = I_{dl} = R_{ct} C_{dl} \frac{d^2 q_{ct}}{dt^2}$  \hspace{1cm} (A1)

2. Currents are equal in series:

   $\therefore I_{ct} + I_{dl} = I_T$  \hspace{1cm} (A3)

   $\therefore \frac{dq_{ct}}{dt} + \frac{dq_{dl}}{dt} = \frac{dq_T}{dt}$  \hspace{1cm} (A4)

3. Voltage across Randles equivalent circuit equals initial voltage across charged capacitor less the voltage discharged:
\[
\therefore V_g = I_g R_\Omega + I_{ct} R_{ct} = V_g - \frac{q_g}{C_g} \quad \quad \quad \quad \quad (A5)
\]

\[
\therefore \frac{dq_{ct}}{dt} R_{ct} + \frac{dq_{di}}{dt} R_{ct} = V_g - \frac{q_{ct} + q_{di}}{C_g} \quad \quad \quad \quad \quad (A6)
\]

Substitute Equation (A4) into Equation (A6):

\[
\therefore \left( \frac{dq_{ct}}{dt} + \frac{dq_{di}}{dt} \right) R_{ct} + \frac{dq_{ct}}{dt} R_{ct} = V_g - \frac{q_{ct} + q_{di}}{C_g} \quad \quad \quad \quad \quad (A7)
\]

Substitute Equations (A1) and (A2) into Equation (A7):

\[
\therefore \left( \frac{dq_{ct}}{dt} + R_{ct} C_{di} \frac{d^2 q_{ct}}{dt^2} \right) R_{ct} + \frac{dq_{ct}}{dt} R_{ct} = V_g - \frac{q_{ct}}{C_g} - \frac{R_{ct} C_{di}}{C_g} \frac{dq_{ct}}{dt} \quad \quad \quad \quad \quad (A8)
\]

This is a second order differential equation of the form:

\[
\therefore \frac{d^2 y}{dx^2} + b \frac{dy}{dx} + cy = d
\]

Firstly solve:

\[
\therefore \frac{d^2 y}{dx^2} + b \frac{dy}{dx} + cy = 0
\]

Let \( y \) be of form \( e^{kx} \), so:
\[
\frac{dy}{dx} = ke^{kx}, \quad \frac{d^2y}{dx^2} = k^2 e^{kx}
\]
\[\therefore k^2 e^{kx} + bke^{kx} + ce^{kx} = 0\]
\[\therefore e^{kx}(k^2 + bk + c) = 0\]

This is a quadratic equation, with solutions:

\[k = \frac{-b \pm \sqrt{b^2 - 4c}}{2}\]

(A9)

Using Equation (A9) to solve Equation (A8):

\[k = \frac{-\left( R_\Omega C_g + R_{ct} C_g + R_{ct} C_{di} \right) \pm \sqrt{\left( R_\Omega C_g + R_{ct} C_g + R_{ct} C_{di} \right)^2 - 4 \frac{R_{ct} C_{di} R_\Omega C_g}{R_{ct} C_{di} R_\Omega C_g}}}{2}\]

(A10)

Let \(k_1\) and \(k_2\) be the two solutions, then:

\[q_{ct} = Ae^{k_1t} + Be^{k_2t} + D\]

Considering the constant \(D\) only:

\[\frac{dq_{ct}}{dt} = 0 \quad \text{and} \quad \frac{d^2q_{ct}}{dt^2} = 0\]

\[\therefore \text{From Equation (A8):}\]
\[
0 + 0 \left( \frac{R_0 C_g + R_c C_g + R_d C_{dl}}{R_c C_{dl} R_{\Omega} C_g} \right) + \frac{D}{R_c C_{dl} R_{\Omega} C_g} = \frac{V_g}{R_c C_{dl} R_{\Omega}}
\]
\[
\therefore D = C_g V_g
\]
\[
\therefore q_{ct} = A e^{k_1 t} + B e^{k_2 t} + C_g V_g
\]

(A11)

No charge has passed through the circuit at \(t = 0\), i.e. \(q_{ct} = 0\) at \(t = 0\).

\[
\therefore q_{ct0} = A + B + C_g V_g = 0
\]
\[
\therefore B = -A - C_g V_g
\]

(A12)

Also, from Equation (A11):

\[
\frac{dq_{ct}}{dt} = I_{ct} = k_1 A e^{k_1 t} + k_2 B e^{k_2 t}
\]

(A13)

\[
\frac{d^2 q_{ct}}{dt^2} = k_1^2 A e^{k_1 t} + k_2^2 B e^{k_2 t}
\]

Substitute Equation (A13) into Equation (A1):

\[
\therefore q_{dl} = R_c C_{dl} (k_1 A e^{k_1 t} + k_2 B e^{k_2 t})
\]

(A14)

No charge has passed through the circuit at \(t = 0\), i.e. \(q_{dl} = 0\) at \(t = 0\).

\[
\therefore q_{dl(t=0)} = R_{\Omega} C_{dl} (k_1 A + k_2 B) = 0
\]
\[
\therefore k_1 A + k_2 B = 0
\]

(A15)

Substitute Equation (A12) into Equation (A15):

\[
\therefore k_1 A + k_2 \left(-A - C_g V_g\right) = 0
\]
\[
\therefore (k_1 - k_2) A = k_2 C_g V_g
\]
\[ A = \frac{k_2 C_g V_g}{k_1 - k_2} \]  \hspace{1cm} (A16)

Substitute Equation (A16) into Equation (A12):

\[ B = -\frac{k_2 C_g V_g}{k_1 - k_2} - C_g V_g = \frac{k_1 C_g V_g}{k_2 - k_1} \]  \hspace{1cm} (A17)

We have now solved for \( k_1, k_2, A, B \) and \( D \) in terms of \( R_\Omega, R_{ct}, C_{dl}, C_g \) and \( V_g \), so we can now calculate \( I_{ct} \) (from Equation (A13)), \( I_{dl} \) (from Equation (A2)), \( I_T \) (from Equation (A3)) and \( V_T \) (from Equation (A5)):

\[ I_T = \frac{k_1 k_2 C_g V_g}{k_1 - k_2} \left[ e^{k_2 t} (1 + k_1 R_{ct} C_{dl}) - e^{k_1 t} (1 + k_2 R_{ct} C_{dl}) \right] \]  \hspace{1cm} (A18)

\[ V_T = \frac{k_1 k_2 C_g V_g}{k_1 - k_2} \left[ e^{k_2 t} (R_\Omega + R_{ct} + k_1 R_{ct} R_\Omega C_{dl}) - e^{k_1 t} (R_\Omega + R_{ct} + k_2 R_{ct} R_\Omega C_{dl}) \right] \]  \hspace{1cm} (A19)
APPENDIX B

Derivation of equations for bipolar capacitor pulse through Randles equivalent circuit

\[ I_T \quad V_T \]

The equations for \( I_T \) and \( V_T \) can be solved in the same manner as performed previously in Appendix A, however some modifications need to be made. At the start of the negative pulse, there is a residual charge \( q_{dl} \) on the capacitor \( C_{dl} \) (i.e. \( q_{dl0} \neq 0 \)), \( q_{ct} = 0 \) because the resistor \( R_{ct} \) retains no charge, and \( q_T = 0 \) because the second capacitor has not commenced discharging. This means that, more correctly, the amount of charge discharged by either capacitor is:

\[ q_T = q_{ct} + q_{dl} - q_{dl0} \]  \hspace{1cm} (B1)

The equations derived in Appendix A are a special case where \( q_{dl0} = 0 \). Thus, where \( q_{dl0} \neq 0 \), Equations (A7) and (A8) become:

\[ \frac{dq_{ct}}{dt} + \frac{dq_{dl}}{dt} R_{\Omega} + \frac{dq_{ct}}{dt} R_{ct} = V_g - \frac{q_{ct} + q_{ct} - q_{dl0}}{C_g} \]  \hspace{1cm} (B2)

\[ \frac{d^2 q_{ct}}{dt^2} + \frac{dq_{ct}}{dt} \left( \frac{R_{\Omega} C_g + R_{ct} C_g + R_{ct} C_{dl}}{R_{ct} C_{dl} R_{\Omega} C_g} \right) + \frac{q_{ct}}{R_{ct} C_{dl} R_{\Omega} C_g} = \frac{V_g C_g + q_{dl0}}{R_{ct} C_{dl} R_{\Omega} C_g} \]  \hspace{1cm} (B3)

Solving the second order differential equation for \( k_1 \) and \( k_2 \) is unchanged, however Equation (A11) becomes:
\[ q_{ct} = Ae^{k_1 t} + Be^{k_2 t} + C_g V_g + q_{dl0} \]  
\[ \text{(B4)} \]

Then, using \( q_{ct} = 0 \) at \( t = 0 \) and \( q_{dl} = q_{dl0} \) at \( t = 0 \), Equations (A16) and (A17) become:

\[
A = \frac{k_2 (C_g V_g + q_{dl0}) + \frac{q_{dl0}}{R_{ct} C_{dl}}}{k_1 - k_2} \tag{B5}
\]

\[
B = \frac{k_1 (C_g V_g + q_{dl0}) + \frac{q_{dl0}}{R_{ct} C_{dl}}}{k_2 - k_1} \tag{B6}
\]

Equations (A18) and (A19) for \( I_T \) and \( V_T \) now become:

\[
I_T = \frac{1}{k_1 - k_2} \left[ k_1 e^{k_1 t} \left( k_2 (C_g V_g + q_{dl0}) + \frac{q_{dl0}}{R_{ct} C_{dl}} \right) \left( 1 + k_1 R_{ct} C_{dl} \right) \right. \\
- k_2 e^{k_2 t} \left. \left( k_1 (C_g V_g + q_{dl0}) + \frac{q_{dl0}}{R_{ct} C_{dl}} \right) \left( 1 + k_2 R_{ct} C_{dl} \right) \right] \tag{B7}
\]

\[
V_T = \frac{1}{k_1 - k_2} \left[ k_1 e^{k_1 t} \left( k_2 (C_g V_g + q_{dl0}) + \frac{q_{dl0}}{R_{ct} C_{dl}} \right) \left( R_{\Omega} + R_{ct} + k_1 R_{ct} R_{\Omega} C_{dl} \right) \right. \\
- k_2 e^{k_2 t} \left. \left( k_1 (C_g V_g + q_{dl0}) + \frac{q_{dl0}}{R_{ct} C_{dl}} \right) \left( R_{\Omega} + R_{ct} + k_2 R_{ct} R_{\Omega} C_{dl} \right) \right] \tag{B8}
\]
APPENDIX C

Simplification of Equation (10.2) for the voltage due to a single capacitor pulse in order to calculate $C_g$.

This requires a simplification for $k$ (Equation (A10)), which is repeated here:

$$
k = \frac{-\left(\Omega C_g + R_{ct} C_{dt} + R_{ct} C_{dl}\right) \pm \sqrt{\left(\Omega C_g + R_{ct} C_{dt} + R_{ct} C_{dl}\right)^2 - 4R_{ct} C_{dt} R_{ct} C_{dl}}}{2R_{ct} C_{dt} R_{ct} C_{dl}} \quad (C1)
$$

In an industrial aluminium reduction cell, $R_{ct} \gg \Omega$ (Table 10.3). Therefore, equations with $R_{ct}$ in the denominator in Equation (C1) can be discounted, since they tend to zero.

$$
\therefore k \approx -\frac{1}{2R_{ct} C_{dt}} - \frac{1}{2R_{ct} C_{dl}} - \frac{1}{2R_{ct} C_{g}} \pm \frac{1}{2} \sqrt{\frac{1}{R_{ct}^2 C_{dt}^2} + \frac{1}{R_{ct}^2 C_{dl}^2} + \frac{1}{R_{ct}^2 C_{g}^2}} + \frac{2}{R_{ct} \Omega C_{dt} C_{dl} + \frac{2}{R_{ct} \Omega C_{g} C_{dl}}} \quad (C2)
$$

If $k_1$ is the negative solution, then:

$$
\therefore k_1 \equiv -\frac{C_g + C_{dt}}{R_{ct} C_g C_{dt}} \quad (C2)
$$

$k_2$ can be calculated using Vieta’s formula:

$$
k_1 k_2 = \frac{c}{a} \quad (C3)
$$
From Equation (A8), \( a = 1 \) and \( c = \frac{1}{R_{ct}R_{\Omega}C_gC_{dl}} \)

\[ : k_2 \equiv \frac{1}{R_{ct}R_{\Omega}C_gC_{dl}} \left(- \frac{R_{\Omega}C_gC_{dl}}{C_g + C_{dl}} \right) = - \frac{1}{R_{ct}(C_g + C_{dl})} \quad (C4) \]

Substituting Equations (C2) and (C4) into Equation (A19) gives:

\[ V_t \equiv \left( \frac{C_gV_g(C_g + C_{dl})}{R_{\Omega}C_gC_{dl} - R_{ct}(C_g + C_{dl})^2} \right) \left[ e^{k_1t} \left( R_{\Omega} + \frac{R_{ct}C_{dl}}{C_g} \right) - e^{k_2t} \left( R_{ct} + \frac{R_{\Omega}C_g}{C_g + C_{dl}} \right) \right] \]

Continuing to assume \( R_{ct} \gg R_{\Omega} \), this can be further simplified to:

\[ V_t \equiv \left( - \frac{C_gV_g}{R_{ct}(C_g + C_{dl})} \right) \left[ e^{k_1t} \left( R_{t} + \frac{R_{ct}C_{dl}}{C_g} \right) - e^{k_2t} \left( R_{ct} + \frac{R_{\Omega}C_g}{C_g + C_{dl}} \right) \right] \quad (C5) \]

In the simulations to date, \( C_{dl} = 3 \text{ F} \) and it was found that a relatively low value of \( C_g \) (e.g. \( 0.1 \text{ F} \)) was required to get the voltage to decay close to zero. Therefore it could be reasonable to assume that a requirement is \( C_g \ll C_{dl} \). Therefore Equations (C2) and (C4) for \( k_1 \) and \( k_2 \) can be simplified to:

\[ k_1 \equiv - \frac{1}{R_{\Omega}C_g} \quad (C6) \]

\[ k_2 \equiv - \frac{1}{R_{ct}C_{dl}} \quad (C7) \]

Substituting Equations (C6) and (C7) into Equation (C5) and continuing to assume \( R_{ct} \gg R_{\Omega} \) gives:

\[ V_t \equiv \left( - \frac{C_gV_g}{R_{ct}C_{dl}} \right) \left[ e^{\frac{t}{R_{ct}C_g}} \left( R_{ct}C_{dl} \right) - e^{\frac{t}{R_{ct}C_{dl}}} \left( R_{ct} \right) \right] \]
\[ V_f \equiv V_g \left[ e^{-\frac{t}{R_\alpha C_f}} + \left( \frac{C_g}{C_{dl}} \right) e^{-\frac{t}{R_\alpha C_d}} \right] \]  

(C8)
APPENDIX D

Derivation of equations for bipolar capacitor pulse through Randles equivalent circuit, with capacitor $C_{dl}$ having an additional resistance $R_{dl}$.

The presence of $R_{dl}$ changes the equations calculated for a bipolar capacitor pulse in Appendix B, so new equations need to be derived as follows.

1. Voltages are equal in parallel:

$$\therefore V_{ct} = V_{dl}$$

$$\therefore I_{ct} R_{ct} = \frac{q_{dl}}{C_{dl}} + I_{dt} R_{dl}$$

$$\therefore \frac{dq_{ct}}{dt} R_{ct} = \frac{q_{dl}}{C_{dl}} + \frac{dq_{dl}}{dt} R_{dl}$$  \hspace{0.5cm} (D1)

2. Currents are equal in series:

$$\therefore I_{ct} + I_{dt} = I_{r}$$  \hspace{0.5cm} (D2)

$$\therefore \frac{dq_{ct}}{dt} + \frac{dq_{dl}}{dt} = \frac{dq_{r}}{dt}$$  \hspace{0.5cm} (D3)

3. Voltage across Randles equivalent circuit equals initial voltage across charged capacitor less the voltage discharged:
\[
\therefore V_T = I_T R_{\Omega} + I_{ct} R_{ct} = V_g - \frac{q_T}{C_g} \tag{D4}
\]

\[
\therefore \frac{dq_T}{dt} R_{\Omega} + \frac{dq_{ct}}{dt} R_{ct} = V_g - \frac{q_T + q_{dl} - q_{dl0}}{C_g} \tag{D5}
\]

Substitute Equation (D3) into Equation (D5):

\[
\therefore \left( \frac{dq_{dl}}{dt} + \frac{dq_{ct}}{dt} \right) R_{\Omega} + \frac{dq_{ct}}{dt} R_{ct} = V_g - \frac{q_T + q_{dl} - q_{dl0}}{C_g} \tag{D6}
\]

Substitute Equation (D1) into Equation (D6):

\[
\therefore \left( \frac{dq_{dl}}{dt} + \frac{q_{dl}}{C_{dl} R_{ct}} + \frac{dq_{dl}}{dt} R_{ct} \right) R_{\Omega} + \left( \frac{q_{dl}}{C_{dl} R_{ct}} + \frac{dq_{dl}}{dt} R_{ct} \right) R_{ct} = V_g - \frac{q_T + q_{dl} - q_{dl0}}{C_g} \tag{D7}
\]

Differentiate Equation (D7) with respect to \( t \):

\[
\therefore \frac{d^2 q_{dl}}{dt^2} \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) + \frac{dq_{dl}}{dt} \left( \frac{C_g R_{\Omega} + C_g R_{ct} + C_{dl} R_{ct}}{C_{dl} C_g R_{ct}} \right)
\]

\[
+ \frac{1}{C_g} \frac{dq_{ct}}{dt} = 0
\]

\[
\therefore \frac{d^2 q_{dl}}{dt^2} \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) + \frac{dq_{dl}}{dt} \left( \frac{C_g R_{\Omega} + C_g R_{ct} + C_{dl} R_{ct}}{C_{dl} C_g R_{ct}} \right)
\]

\[
+ \frac{1}{C_g} \left( \frac{q_{dl}}{C_{dl} R_{ct}} + \frac{dq_{dl}}{dt} R_{ct} \right) = 0
\]

\[
\therefore \frac{d^2 q_{dl}}{dt^2} \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) + \frac{dq_{dl}}{dt} \left( \frac{C_g R_{\Omega} + C_g R_{ct} + C_{dl} R_{ct} + C_{dl} R_{dl}}{C_{dl} C_g R_{ct}} \right)
\]
\[ + \frac{q_{dl}}{C_{dl}C_g R_{ct}} = 0 \]

\[ \therefore \frac{d^2 q_{dl}}{dt^2} + \frac{dq_{dl}}{dt} \left( \frac{C_s R_\Omega + C_g R_{ct} + C_{dl} R_{ct} + C_{dl} R_{dl}}{C_{dl} C_g \left(R_\Omega R_{ct} + R_{dl} R_\Omega + R_{dl} R_{ct}\right)} \right) + \frac{q_{dl}}{C_{dl} C_g \left(R_\Omega R_{ct} + R_{dl} R_\Omega + R_{dl} R_{ct}\right)} = 0 \]

\[ \therefore \frac{d^2 q_{dl}}{dt^2} + \frac{dq_{dl}}{dt} \left( \frac{C_s R_\Omega + C_g R_{ct} + C_{dl} R_{ct} + C_{dl} R_{dl}}{x} \right) + \frac{q_{dl}}{x} = 0 \quad (D8) \]

Where \( x = C_{dl} C_g \left(R_\Omega R_{ct} + R_{dl} R_\Omega + R_{dl} R_{ct}\right) \)

As per Chapter 10.7, this is a second order differential equation of the form:

\[ \therefore \frac{d^2 y}{dx^2} + b \frac{dy}{dx} + cy = 0 \]

Let \( y \) be of form \( e^{kx} \), so:

\[ \frac{dy}{dx} = k e^{kx}, \frac{d^2 y}{dx^2} = k^2 e^{kx} \]

\[ \therefore k^2 e^{kx} + b k e^{kx} + c e^{kx} = 0 \]

\[ \therefore e^{kx}(k^2 + bk + c) = 0 \]

This is a quadratic equation, with solutions:

\[ k = \frac{-b \pm \sqrt{b^2 - 4c}}{2} \quad (D9) \]

Using Equation (D9) to solve Equation (D8):

\[ k = -\left( \frac{C_s R_\Omega + C_g R_{ct} + C_{dl} R_{ct} + C_{dl} R_{dl}}{x} \right) \pm \sqrt{\left( \frac{C_s R_\Omega + C_g R_{ct} + C_{dl} R_{ct} + C_{dl} R_{dl}}{x} \right)^2 - \frac{4}{x}} \]
\[ k = \frac{-\left(C_s R_\Omega + C_s R_{ct} + C_{dl} R_{ct} + C_{dl} R_{di}\right) \pm \sqrt{\left(C_s R_\Omega + C_s R_{ct} + C_{dl} R_{ct} + C_{dl} R_{di}\right)^2 - 4x}}{2x} \]

\[ \therefore k = \left[ -\left(C_s R_\Omega + C_s R_{ct} + C_{dl} R_{ct} + C_{dl} R_{di}\right) \right. \]

\[ \pm \sqrt{\left(C_s R_\Omega + C_s R_{ct} + C_{dl} R_{ct} + C_{dl} R_{di}\right)^2 - 4C_{dl} C_s \left(R_\Omega R_{ct} + R_{di} R_\Omega + R_{di} R_{ct}\right)} \]

\[ \left. 2C_{di} C_s \left(R_\Omega R_{ct} + R_{di} R_\Omega + R_{di} R_{ct}\right) \right] \]

Let \( k_1 \) and \( k_2 \) be the two solutions, then:

\[ q_{dl} = Ae^{k_1 t} + Be^{k_2 t} \]  \hspace{1cm} (D10)

There is residual charge on the capacitor \( C_{dl} \) at \( t = 0 \), i.e. \( q_{dl} = q_{dl0} \) at \( t = 0 \).

\[ \therefore A + B = q_{dl0} \]

\[ \therefore B = q_{dl0} - A \]  \hspace{1cm} (D11)

Differentiate Equation (D10) with respect to \( t \):

\[ \therefore \frac{dq_{dl}}{dt} = k_1 Ae^{k_1 t} + k_2 Be^{k_2 t} \]  \hspace{1cm} (D12)

Substitute Equation (D10) and Equation (D12) into Equation (D1):

\[ \therefore \frac{dq_{ct}}{dt} = \frac{Ae^{k_1 t} + Be^{k_2 t}}{C_{dl} R_{ct}} + \left(k_1 Ae^{k_1 t} + k_2 Be^{k_2 t}\right) \frac{R_{di}}{R_{ct}} \]  \hspace{1cm} (D13)

Integrate Equation (D13) with respect to \( t \):

\[ \therefore q_{ct} = \frac{Ae^{k_1 t} + Be^{k_2 t}}{k_1 C_{dl} R_{ct}} + \left(Ae^{k_1 t} + Be^{k_2 t}\right) \frac{R_{di}}{R_{ct}} + D \]  \hspace{1cm} (D14)
No charge has passed through the circuit at $t = 0$, i.e. $q_{ct0} = 0$.

\[
\frac{A + B}{k_1} + \frac{k_2}{C_{dl} R_{ct}} + (A + B) \frac{R_{dl}}{R_{ct}} + D = 0 \tag{D15}
\]

Substitute Equation (D11) into Equation (D15):

\[
\frac{A + q_{dl0} - A}{k_1} + \frac{k_2}{C_{dl} R_{ct}} + (A + q_{dl0} - A) \frac{R_{dl}}{R_{ct}} + D = 0
\]

\[
∴ D = -q_{dl0} \frac{R_{dl}}{R_{ct}} - \frac{A + q_{dl0} - A}{k_1} \frac{k_2}{C_{dl} R_{ct}}
\]

\[
∴ D = -q_{dl0} \frac{R_{dl}}{R_{ct}} \frac{Ak_2 + q_{dl0}k_1 - Ak_1}{C_{dl} R_{ct}} \tag{D16}
\]

Substitute Equations (D11) and (D12) into Equation (D7), and use $q_{dl0} = 0$ and $q_{ct0} = 0$ at $t = 0$.

\[
(\bar{k}_1 + k_2 B) \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) + q_{dl0} \left( \frac{C_{g} R_{\Omega} + C_{g} R_{ct} + C_{dl} R_{ct}}{C_{dl} C_{g} R_{ct}} \right) = V_g + q_{dl0} \frac{R_{ct}}{C_{g}}
\]

\[
(\bar{k}_1 + k_2 B) \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) + q_{dl0} \left( \frac{C_{g} R_{\Omega} + C_{g} R_{ct} + C_{dl} R_{ct}}{C_{dl} C_{g}} \right) = V_g R_{ct} + q_{dl0} \frac{R_{ct}}{C_{g}}
\]

\[
(\bar{k}_1 + k_2 B) \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) = V_g R_{ct} - q_{dl0} \frac{R_{\Omega} + R_{ct}}{C_{dl}}
\]

\[
(\bar{k}_1 + k_2 (q_{dl0} - A)) \left( \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{R_{ct}} \right) = V_g R_{ct} - q_{dl0} \frac{R_{\Omega} + R_{ct}}{C_{dl}}
\]

\[
V_g R_{ct} - q_{dl0} \frac{R_{\Omega} + R_{ct}}{C_{dl}} = -k_2 q_{dl0}
\]

\[
∴ A = \frac{R_{\Omega} R_{ct} + R_{dl} R_{\Omega} + R_{dl} R_{ct}}{k_1 - k_2}
\]

And similarly:
\[ V_0 R_{ct} - q_{d10} \left( \frac{R_\Omega + R_{ct}}{C_{dl}} \right) \]
\[ \therefore B = \frac{R_\Omega R_{ct} + R_{dl} R_\Omega + R_{dl} R_{ct}}{k_2 - k_1} \]

We have now solved for \( k_1, k_2, A, B \) and \( D \) so we can now calculate \( I_{ct} \) (from Equation (D13)), \( I_{dl} \) (from Equation (D12)), \( I_T \) (from Equation (D2)) and \( V_T \) (from Equation (D4)).

\[ \therefore I_T = A e^{k_1 t} \left( k_1 + \frac{k_1 R_{dl}}{R_{ct}} + \frac{1}{R_{ct} C_{dl}} \right) + B e^{k_2 t} \left( k_2 + \frac{k_2 R_{dl}}{R_{ct}} + \frac{1}{R_{ct} C_{dl}} \right) \]

\[ \therefore V_T = A e^{k_1 t} \left( k_1 R_\Omega + \frac{k_1 R_{dl} (R_\Omega + R_{ct})}{R_{ct}} + \frac{R_\Omega + R_{ct}}{R_{ct} C_{dl}} \right) \]
\[ + B e^{k_2 t} \left( k_2 R_\Omega + \frac{k_2 R_{dl} (R_\Omega + R_{ct})}{R_{ct}} + \frac{R_\Omega + R_{ct}}{R_{ct} C_{dl}} \right) \]
## APPENDIX E

### ACD: 40mm

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### ACD: 80mm

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<th>t-stat</th>
<th>P-value</th>
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REFERENCES


44. Kisza, A., Thonstad, J. and Eidet, T. 1996. Impedance Study of the Kinetics and Mechanism of the Anodic Reaction on Graphite Anodes in Saturated Cryolite-


