A NOVEL PULSATING CURRENT TECHNIQUE USED IN THE STUDY
OF PLATINUM AND MOLYBDENUM ELECTRODES IN MOLTEN
SILICATES, BORATES AND PHOSPHATES

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The time to oxygen evolution at platinum electrodes in mol­
ten soda lime silicate glass and sodium disilicate, diborate
and diphosphate has been measured using a pulsating current
method originally introduced by Hickling. At 0.083A/cm²
and 1200°C the times measured were 50, 20, 20 and 9msec, res­
pectively, and these varied hardly at all with temperature,
but decreased with increasing current density. The reason
for the delay using the silicate compositions was shown to
be the periodic formation and removal of a monomolecular la­
ger of PtO₂ on the anode. This did not occur in the bor­
ate to the same extent, probably because of the alloying of
platinum with boron. In the phosphate melts the platinum
dissolved as phosphate, probably with the formation of thick
salt films on the electrode. At a molybdenum anode in sil­
cicate glass the voltage rose almost immediately to oxygen
evolution on the application of the current.

During an investigation into the ac electrolysis of molten soda
lime silicate glass at 1350°C and 0.6A/cm² using platinum electrodes
it was found that the platinum corroded extensively at a frequency
of 50Hz, but not at a frequency of 500Hz(1). This was tentatively
ascribed to the formation of oxygen bubbles round the electrode
during the longer, 10msec, positive half cycle time at 50Hz, but not
during the shorter, 1msec, positive half cycle time at 500Hz. It
was important to decide this question by a direct measurement of the
time taken to oxygen evolution and this measurement was carried out
using an adaptation of an oscillographic pulsating current method
originally due to Hickling(2).

It was found that the time to oxygen evolution at 1350°C and
0.6A/cm² was 2.6msec at a platinum anode and so the oxygen gas does
not have time to form during the 1msec half cycle time of the 500Hz ac
input, but it does have time to form during the 10msec half cycle
time of the 50Hz ac input(3). Thus the corrosion results above
receive a logical explanation.

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Since the method had proved successful in settling this question, the measurements were extended to different temperatures in the range 900°C to 1350°C using current densities from 0.017 to 1.333 A/cm². In addition, similar measurements were made in other systems such as sodium disilicate, diborate and diphosphate melts, (4) and at molybdenum electrodes in soda lime silicate glass with, and without, added sulphate refiner (5).

The above measurements of time to oxygen evolution were made using the internal time base of the oscilloscope, but it was also possible to record oscillograms of voltage against quantity of electricity passed. Much further information on the reactions occurring before oxygen evolution in all these systems was obtained using this technique: measurements were made of the electrical double layer capacity in the initial stages of polarisation; of the thickness of any oxide layer formed prior to oxygen evolution; of the reproducible values of oxygen evolution potential.

Finally, these results were compared with those obtained in the same electrolytes using a conventional, single pulse method. In general, the pulsating current method gave much more information on the electrochemical reactions occurring than did the single pulse method. However, the single pulse method was useful in giving information on one particular aspect of the polarisation: its decay time. This was extremely short at the electrodes of molybdenum in silicate glass melts, but at platinum electrodes the decay was slower and varied with the nature of the electrolyte.

**EXPERIMENTAL**

Figure 1 is a diagram of the circuit embodying Hickling's method but using modern, solid state components. The main loop is the one on the left of the diagram and consists of a constant current unit, a capacitor and the cell itself. Across the capacitor-cell combination is placed a thyristor with its gate biased so that it trips into conduction when a pre-determined voltage is applied to its collector.

In operation a constant, preset current is passed through the capacitor and cell in series, from the constant current unit and the voltage on the plates of the capacitor rises. Eventually, the voltage on the upper plate of the capacitor reaches that required to trigger the thyristor into conduction, and the thyristor thus acts as a short circuit for the capacitor and the cell. Then the capacitor discharges a quantity of electricity exactly equal to that originally passed, flowing rapidly through the cell in the reverse direction. This process should repeat itself indefinitely and, using a thyratron valve as in Hickling's original circuit, it does. However, this cannot happen with the thyristor because once in conduction it cannot switch itself off while current is flowing from the constant current unit. It is the function of the monostable oscillator in the right hand loop to overcome this. This detects the large discharge through
the thyristor when it occurs and then sends a pulse to the constant
current unit stopping it for a pre-determined blanking period, and thus
allowing the thyristor to switch off. At the end of the pulse the
constant current unit switches on again and the whole cycle of charge
and discharge repeats itself indefinitely.

The voltage between the electrode in the cell which is being
studied and a suitable reference electrode is fed to the Y-plates of
the oscilloscope and the voltage across the capacitor (which is
exactly proportional to the quantity of electricity passed at any
time) is applied to the X-plates. Under these conditions the trace
on the oscilloscope screen represents the variation of the potential
of the working electrode with the quantity of electricity passed
through the cell (V/q oscillograms). Alternatively, the internal
time base of the oscilloscope may be used to record the X-axis displ­
acement and then gives the time for any electrochemical reaction to
occur directly (V/t oscillograms).

In all the experiments, starting with fresh electrodes, in the
present investigation, the trace on the oscilloscope screen moved
downwards initially when the pulsating current was first switched on
indicating some change in the surface of the electrode. After a few
seconds, however, the trace stabilised and then remained stationary
for hours and days at a time, and could be photographed at leisure.
This fact, that the oscilloscope tracks are stationary, means that
the technique is isolating the true and reproducible part of the
polarisation, and that exactly the same change of potential is brought
about by charging the electrode as discharging it — that is, there is
no irreversible loss of electro-chemically active material from the
electrode. It means that the electrode is brought back to its orig­
inal state with no accidental variation in its condition at the end
of every cycle: and this is the unique feature of the method com­
pared with conventional, single pulse methods where the initial state
of the electrode is not usually clearly defined and measurements are
made on transients.

In order to illustrate some of the general characteristics of
the tracks observed with this circuit we give a V/t oscilloscope
trace in Figure 4(a) using a 10Ω resistor in place of the cell in
Figure 1. The upper track shows the charge and discharge of the
100μF capacitor C with the oscilloscope probe placed at monitor point
MP3; the lower track shows the current through the 10Ω resistor
obtained by placing the oscilloscope probe at monitor point MP1, just
above the small, 0.1Ω resistor used for monitoring the current.

We consider the first pulse at the start of the linear rise in
voltage across the capacitor at the point denoted by the letter "s"
on both the horizontal and the vertical axes. The current is switch­
ed on and continues at a constant value as the voltage across the cap­
acitor rises. Eventually the thyristor goes into conduction, the
voltage across the capacitor drops and a large current — shown by the
spike in the track — flows through the 10Ω resistor in the opposite
direction. This is followed by the blanking period during which the
current is switched off and the capacitor voltage is constant.
Next the current is switched on again and the capacitor voltage starts to rise for the second pulse. The reader should note that the switch-on point of the current and the start of the capacitor voltage rise coincide and occur at the end of the blanking period in each case.

The constant current unit consisted of two Darlington pairs made up from two MJE 340 and two MJE 350 transistors, respectively, and capable of supplying a maximum current of 500mA; the thyristor was a BTY-79 type; the monostable oscillator was a COSMOS 4098 chip. Any of a bank of four electrolytic capacitors of value 50, 100, 250 or 500µF could be switched into the circuit, but the 50 and 100µF ones were the capacitors most used for the measurements. These could all be by-passed to allow a constant current to flow through a dummy 100Ω load, of approximately the same resistance as the cell, in order to preset the constant current unit; and in some cases also to pass dc through the cell itself. With certain settings of the thyristor triggering and the blanking period controls the equipment could cease to operate, but could be restarted by changing both these controls to a more suitable value and then pressing the reset button shown just beneath the constant current unit. This broke the circuit temporarily, allowing the thyristor to switch off and the pulse cycle to be re-established.

The circuit used in the second, conventional single pulse method is shown in Figure 2. The most important component is the relay and this controls those components in the left hand loop of the diagram: the constant current unit, the cell and the load. When the relay is at position 3 the preset current from the constant current unit flows through the cell; on the other hand, when the relay is at position 2 the cell discharges through the load. The action of the relay is itself controlled by the monostable oscillator on the right hand side of the diagram. When the start button, S1, is pressed, the monostable oscillator below it emits a pulse of preset length and moves the relay contact from position 2 to position 3. Current from the preset constant current unit flows through the cell and the 0.1Ω current monitoring resistor for the duration of the preset pulse. At the end of the set pulse the relay contact moves back from position 3 to position 2, and the cell is allowed to discharge through the load, which may be of any sized resistor or a short circuit.

The shape of the pulse and the voltage decay may be examined by placing an oscilloscope across any two of the cell electrodes and the current through the cell and load monitored by placing a probe just above the 0.1Ω resistor. The residual voltage on the cell electrodes may be measured over long periods, if required, by opening the switch, S3, and reading off the voltage on the digital voltmeter.

The constant current unit consisted of the usual two Darlington pairs made using MJE 340 and MJE 350 transistors, and the monostable oscillator was a COSMOS 4098 chip fed into a 4049 buffer amplifier chip. The relay was a mercury wetted type 97-1-C-12-7 with a fast switching speed of 250µsec.
A Tektronix, type 564, storage oscilloscope was used throughout these experiments. To measure the ac resistance of the cell a Wayne Kerr bridge, type B221, driven by a type S121 AF signal generator was used.

A diagram of the electrolysis cell is shown in Figure 3. It consisted of a 100cm³ conical, recrystallised alumina crucible containing 100gm of ground electrolyte. The electrodes were 0.625mm diameter platinum wires fitted through small, 1mm diameter holes in the square, 2mm thick, pure alumina top plate. The wires were crimped and held in position in this plate by a heavier, square 1cm thick Mullite block placed over them.

The length of the wires dipping into the glass was 1.5cm, and this corresponded to an area of 0.3cm². Four wires were inserted into the the cell, three of them being at the apices of an equilateral triangle of side 3cm and the fourth at the mid-point of any one of the sides. This last wire and that at the opposite apex served as reference electrodes, but it was found that there was no measurable difference between the results obtained with the reference electrodes in these different positions, and for most of the experiments the wire at the opposite apex of the triangle was the one most used as reference electrode. The electrodes in the furnace were connected to the electrical equipment by double strands of the same platinum wire twisted round their tops and insulated by alumina beads. The most usual temperatures used were from 900°C to 1400°C, and between electrical experiments the crucible and its contents were kept at 900°C in the silicon carbide furnace in order to minimise corrosion problems.

The wt% composition of the glass used was 69.2 SiO₂, 11.2 Na₂O, 9.3 CaO and 5.3 K₂O; the minor constituents were MgO, BaO, Al₂O₃ and B₂O₃.

The sodium disilicate was made by heating the appropriate amount of silica (Limonges quartz) and AR sodium carbonate in an alumina crucible to 1300°C for 2 hours and then casting on stainless steel. For the sodium diborate, finely ground, commercial borax glass (Fison’s) which had the sodium borate composition was used directly in the alumina cell. The sodium diphosphate was made by heating AR sodium metaphosphate with orthophosphoric acid and casting on stainless steel. Further details of all these preparations are given in reference (4).

When experiments were conducted with molybdenum, precautions had to be taken to protect the metal from the air due to the high reactivity of heated molybdenum with oxygen. First an inert atmosphere of N₂/5% H₂ was provided above the glass in the cell by passing the gas mixture down both channels of a double bored, ¼ inch diameter alumina tube passing through holes in the centre of the Mullite block and the alumina plate. Then the actual molybdenum wires were protected from the air by joining them to platinum connecting wires below the Mullite block and alumina plate and thus in the inert gas atmosphere.
The diameter of the molybdenum wire was 0.12cm, and the electrode area below the glass surface was 0.6cm². The molybdenum metal was 99.9% pure (Materials Research). For further details on the exact procedure used during an experiment the reader is referred to reference (5). The glass used had the composition shown in Table I.

Table I Analysis of Glass with and without Sulphate Refiner (wt%)

|       | SiO₂ | Na₂O | CaO | MgO | Al₂O₃ | K₂O | Fe₂O₃ | SO₃ |
|-------|------|------|-----|-----|-------|-----|-------|-----|
| With Sulphate | 72.6 | 13.0 | 8.3 | 4.1 | 1.0   | 0.6 | 0.117 | 0.24 |
| Sulphate Free  | 73.1 | 12.9 | 8.3 | 4.0 | 1.0   | 0.6 | <0.02 | 0.06 |

Two samples of the glass were examined, one to which sodium sulphate had been added as a refining agent and one to which no sulphate had been added; the SO₃ compositions of the two glasses are given in column 8 of Table I above.

RESULTS

Platinum-Soda Lime Silicate Glass

In Figure 4(b) is shown a V/t oscillogram at a temperature of 1350°C and a current density of 0.6A/cm². The upper trace gives the change of voltage across the cell with time (oscilloscope probe at monitor point MP4 in Figure 1), and the lower trace gives the value of the current during the time of the experiment (second oscilloscope probe at monitor point MP1 in Figure 1).

The first part of the tracks show the large negative currents flowing followed by the blanking periods; next the long horizontal region in the lower current trace illustrates that the current flowing through the cell is constant. When this is first switched on, the voltage shown in the upper track rises, initially, so rapidly that the oscilloscope trace disappears. This rapid rise is then followed by a slower rise until a break in the curve occurs; then there is a further small, slower rise until a plateau is reached when oxygen evolution occurs. The horizontal distance from the start of the current to the point at which the oxygen evolution plateau starts is 1.3 divisions and, since the time base scale is 2msec per division, this represents a time of 2.6msec. It thus takes 2.6msec from the start of the electrolysis for oxygen evolution to be attained.

The initial, extremely rapid rise in voltage following the switch-on is due to the resistance of the glass. From the height of the jump and the constant current density it is calculated to be 8.30, and this is in good agreement with the value of 70 measured at 1000Hz using the ac bridge. In measuring oxygen evolution voltages we ignore this rise due to the glass resistance and start measurements from the beginning of the next, slower voltage rise, visible on the oscillogram. This point is denoted on the photograph by the
letter "s" on both the horizontal and vertical axes and this point, thus specified, will be used as the starting point for all future oscillograms. Under the particular conditions of electrolysis of the present oscillogram the oxygen evolution voltage measured from this starting point to the beginning of the oxygen evolution plateau is about 1.8V, while it is about 2.2V if the measurement is made between the point marked "s" and the end of the plateau when oxygen evolution is occurring freely (see reference(3) for a fuller discussion of this point).

The high temperature and current density were chosen for this experiment because these were the conditions under which the corrosion discussed in reference (1) was occurring. However, for the later, systematic experiments we usually worked at the lower temperature of 1200°C and a current density of 0.083A/cm², and Figure 4(c) shows a V/t oscillogram obtained under these conditions. The general features are similar to those in Figure 4(a), but the time to the start of oxygen evolution is longer - 50msec - and the oxygen evolution voltage is 1.5v, measured across the cell from the working anode to earth for this oscillogram.

It is instructive to compare the three tracks obtained simultaneously with the oscilloscope probes across the various components of the working, auxiliary and reference electrodes. The three tracks shown in Figure 4(d) were obtained with the Y-axis differential amplifiers connected across the working and auxiliary electrodes (upper trace), across the working and platinum reference electrodes (middle trace), and across the reference and auxiliary electrodes (lower trace). The positive oscilloscope probe was connected to the first mentioned electrode in each case. Measurements of the Y-coordinates of these tracks showed that the voltage across the working-auxiliary electrode combination is the sum of those across the working-reference and the reference-auxiliary combination - and this, of course, is to be expected. It should be carefully noted, however, that the track of working against auxiliary electrode is linear after oxygen evolution has started, when the electrode is heavily polarised, and that there is no curvature in opposing senses - positive and negative - in the other two tracks, which there would be if the potential of the reference electrode were changing. Of course, a measurement between a working and a reference electrode is much to be preferred to one between a working and an auxiliary electrode because the track levels off to a steady oxygen evolution value in the former case, but increases continuously in the latter case, as can be seen from Figure 4(d).

A series of measurements of the time to oxygen evolution was carried out, using V/t oscillograms, at current densities ranging from 0.017A/cm² to 1.333A/cm² and temperatures from 900° to 1350°C. The effect of change in current density is shown in Table II; all the measurements were made on tracks with the working electrode coupled to the platinum reference electrode.
Table II Effect of Current Density on Time to Oxygen Evolution in Soda Lime Silicate Glass at 1200°C

| Current Density A/cm² | Time to Oxygen Evolution msec | Current Density x Time C/apparent cm² |
|-----------------------|-----------------------------|-------------------------------------|
| 0.017                 | 122                         | 2.07 x 10⁻³                         |
| 0.025                 | 120                         | 3.00 x 10⁻³                         |
| 0.033                 | 108                         | 3.56 x 10⁻³                         |
| 0.083                 | 50                          | 4.15 x 10⁻³                         |
| 0.167                 | 20                          | 3.34 x 10⁻³                         |
| 0.250                 | 14                          | 3.50 x 10⁻³                         |
| 0.333                 | 10                          | 3.33 x 10⁻³                         |
| 0.500                 | 8                           | 4.03 x 10⁻³                         |
| 0.600                 | 5                           | 3.03 x 10⁻³                         |
| 0.667                 | 7                           | 4.67 x 10⁻³                         |
| 1.000                 | 3                           | 3.00 x 10⁻³                         |
| 1.333                 | 1.4                         | 1.87 x 10⁻³                         |

The time to oxygen evolution decreases with increasing current density but, surprisingly, the product of the current density and the time remains fairly constant apart from the values at the highest and lowest current densities. A similar type of behaviour has been observed in connection with ac electrolysis in reference (1), and this subject will be examined in the discussion section.

The results obtained when the temperature was varied are shown in Table III. The low current density of 0.025A/cm² was chosen for these experiments because it was difficult to exceed this current density at the lower temperatures.

Table III Effect of Temperature on Time to Oxygen Evolution in Soda Lime Silicate Glass at a Current Density of 0.025 A/cm²

| Temperature °C | Time to Oxygen Evolution msec | Current Density x Time C/apparent cm² |
|---------------|-------------------------------|-------------------------------------|
| 900           | 96                            | 2.40 x 10⁻³                         |
| 1000          | 118                           | 2.95 x 10⁻³                         |
| 1100          | 132                           | 3.30 x 10⁻³                         |
| 1200          | 120                           | 3.00 x 10⁻³                         |
| 1300          | 116                           | 2.90 x 10⁻³                         |
| 1350          | 106                           | 2.65 x 10⁻³                         |
Again the product of current density and time is remarkably constant, apart from the two extreme values at 900°C and 1350°C which are slightly lower. From column 2 it is seen that the time to oxygen evolution also remains fairly constant with change in temperature when the current density is fixed at 0.025A/cm², in contrast to its behaviour with change in current density at constant temperature shown in Table II.

The growth of the voltage across the cell and its decay may also be studied using the second, conventional single pulse circuit of Figure 2. An oscillogram made using this circuit with the probes connected across the cell (upper trace) and also across the 0.1Ω resistor (lower trace) is shown in Figure 4(e); the current density was 0.083A/cm² and a pulse width of 100msec was used. The zero voltage lines for the upper and lower traces are located two and three large divisions, respectively, below the central X-axis line in Figure 4(e), and these are marked out with a zero, "0".

Considering the upper trace, the voltage across the cell rises smoothly with time with none of the breaks in the curve found in the growth curve using the first, pulsating current circuit. The final voltage recorded is about 1.1V - or 0.9V allowing 0.2V off for the voltage drop due to the glass resistance, and this may be taken as an oxygen evolution voltage, although the trace appears not to have stopped rising at this point. It will be recalled from Figure 4(c), using the first circuit, that the start of oxygen evolution was clearly shown 50msec after the commencement of electrolysis. The oxygen evolution voltage of 1.5V recorded then may be compared with the 0.9V found now with the second circuit. It seems that oxygen evolution may not be attained with the 100msec pulse using the second circuit, and this is noteworthy in that it was attained in 50msec using the first, pulsating current circuit.

When the current is switched off the voltage across the cell decays in one of three ways depending on the load resistance into which the cell is discharged: into an open circuit or a 10MΩ resistor (upper trace) the voltage decay is very slow; into a 1Ω resistor (middle trace) the rate of decay increases; finally, if the cell is discharged into a short circuit (lower trace) then the voltage decay is relatively rapid and occurs in about 20msec.

The behaviour of the current during the decay is interesting. Only the trace obtained with the cell short circuited is given, but this shows that the current actually reverses direction during the decay period and appears below the lower zero line before decaying to zero in about 20msec. The decay time of the current into a short circuit does not seem to depend on the current density: Figure 4(f) shows the tracks of growth and decay at four different current densities and the decay time for each is the same.
Whilst the V/t oscillograms give valuable information about the delay time of oxygen evolution, the corresponding V/q oscillograms give more information about the electrochemical reactions occurring at the electrodes. In Figure 4(g) is shown a typical V/q oscillogram at a temperature of 1200°C and a current density of 0.083A/cm². The Y-axis reading gives the voltage across the working-reference electrode combination and the X-axis reading gives the quantity of electricity passed into the capacitor and cell at any particular point.

The oscilloscope trace may be divided into four parts: After the very rapid rise due to the glass resistance the voltage rises nearly linearly (stage 1); at a voltage of about 0.45V there is a break in the curve when the voltage continues to increase at a lower rate (stage 2); then there is a second, more rapid, linear rise (stage 3); finally the oxygen evolution plateau is attained (stage 4). The gradient of the trace in stage 1 may be easily found. Measuring the X-axis displacement and multiplying by the capacity of the capacitor (100μF) gives the charge accumulated in stage 1 as 400μC; dividing by the voltage rise of 0.45V gives a value of 889μC/V for the gradient, or 889μF using the familiar relationship Q = CV for the capacitor. This value of the gradient is usually regarded as the capacity of the double layer at the electrode in the early stage of the electrolysis and, by dividing by 0.3cm², a value of 296μF/apparent cm² is obtained for the double layer capacity under these conditions. Using a similar method the charge accumulated during the next slower stage - stage 2 - may be found and works out at 600μC or 2000μC/apparent cm². The gradient of the graph in stage 3 is found to be 400μC/V or 1333μC/V per apparent cm². Finally, the oxygen evolution voltage is found to be 1.20V measured, of course, from the end of the rapid voltage rise due to the glass resistance.

The various parameters which we have considered are fairly reproducible, and the oxygen evolution voltages particularly so. We measured the various parameters on a sample of 22 different oscillograms at the same current density of 0.083A/cm², photographed at various times during a three week experiment in which the crucible and its contents were cycled many times between 900 and 1350°C. We used the Coefficient of Variation to compare the various parameters. This is the sample standard deviation divided by the mean, and it measures the spread of the individual results; it is expressed as a percentage and is dimensionless.

The parameters considered were the following (with the coefficients of variation in parentheses): the double layer capacity of stage 1 (14.1%); the voltage increase to the start of stage 2 (12.9%); the charge increment during stage 2 (16.9%); the gradient of stage 3 (8.7%); the oxygen evolution voltage (2.32%). Whilst the variation in all the parameters except the oxygen evolution voltage is of the size expected for this type of electrochemical measurement, the value of the coefficient of variation for the oxygen evolution voltage is exceptionally small at 2.3%. Indeed, the calculation of the 95% Confidence Interval of the mean gives a value of (1.21V, 1.19V) and this implies that there is a 95% probability that any sample...
reading of oxygen evolution voltage will be between these two values. For further information on this point see reference (3).

There is another aspect of reproducibility apart from the above: it concerns what happens to the oscillograms after a period of dc polarisation. Figure 4(h) shows successive traces photographed over a period of 1 minute after an initial dc polarisation of 30 seconds at a current density of 0.083 A/cm². The trace is first displaced to the left on the application of the dc but then returns over a period of about 1 min to the original steady position it had on the screen before the dc polarisation was applied. It is known that, provided the glass is not polarised, the oscilloscope tracks are steady and reproducible; but this experiment shows that even if the glass is polarised by direct current, the oscilloscope trace returns to its original position fairly rapidly when the dc polarising current is removed.

The various parameters which we have discussed above were measured at different current densities between 0.017 A/cm² and 1.333 A/cm² at 1200°C, and the results of this work are shown in Table IV:

Table IV Variation in the Parameters of the V/q Oscillograms with Current Density at 1200°C

| Current Density A/cm² | Double Layer Capacity μF/app.cm² | Volts. Inc. to start of stage 2 | Charge Inc. in stage 2 μC/app.cm² | Gradient of stage 3 μC/app.cm²/V | Oxygen Evolution Voltage in stage 4 V |
|-----------------------|----------------------------------|---------------------------------|----------------------------------|---------------------------------|----------------------------------|
| 0.017                 | 2223                             | 0.42                            | 2400                             | 1333                             | 1.16                             |
| 0.025                 | 2540                             | 0.42                            | 2533                             | 1480                             | 1.16                             |
| 0.033                 | 2610                             | 0.46                            | 2333                             | 1480                             | 1.18                             |
| 0.083                 | 2963                             | 0.45                            | 2000                             | 1333                             | 1.20                             |
| 0.167                 | 2267                             | 0.50                            | 1600                             | 1853                             | 1.20                             |
| 0.250                 | 2000                             | 0.60                            | 1200                             | 1840                             | 1.26                             |
| 0.333                 | 2191                             | 0.70                            | 867                              | 1667                             | 1.30                             |
| 0.500                 | 1167                             | 0.80                            | 933                              | 1333                             | 1.40                             |
| 0.667                 | 1003                             | 0.95                            | 800                              | 1500                             | 1.50                             |
| 1.000                 | 800                              | 1.00                            | 667                              | 1067                             | 1.60                             |
| 1.333                 | 667                              | 1.00                            | 800                              | 1333                             | 1.80                             |

In this table the current density range of 0.250 to 0.333 A/cm² seems to form a natural dividing line for the data: below this line most of the parameters are roughly of the same order, but above this limit they vary - for example, the double layer capacity (column 2) starts to decrease at current densities above the range 0.250 - 0.333 A/cm². This is not surprising in view of Figure 4(i) which is a V/q oscillogram at 0.333 A/cm²: the initial part of the track - stage 1 - is curved, and the double layer capacity concept is of doubtful validity under these conditions. On the other hand, the stage 3 part of the trace is still linear, and this is reflected in the relative
constancy of the values in column 5 of Table IV. The charge increment during stage 2, given in column 4, shows a drift downwards above a current density of 0.083A/cm² with the values of roughly the same order below it. The parameters which do show a systematic change are the voltages measured in columns 3 and 6: both the voltage increment to the start of stage 2 and the oxygen evolution voltage increase steadily.

The changes which occurred in the V/q parameters when the temperature was changed were also measured and the results are given in Table V:

| Temperature °C | Double Layer Capacity stage 1 µF/app.cm² | Volts. Inc. to start of stage 2 V | Charge Inc. in stage 2 µC/app.cm² | Gradient of stage 3 µC/app.cm²/V | Oxygen Evolution Voltage in stage 4 V |
|---------------|------------------------------------------|----------------------------------|----------------------------------|---------------------------------|-----------------------------------|
| 900           | 3333                                     | 0.82                             | 600                              | 750                             | 1.50                              |
| 1000          | 3187                                     | 0.67                             | 1467                             | 1000                            | 1.37                              |
| 1100          | 2760                                     | 0.58                             | 2133                             | 1250                            | 1.32                              |
| 1200          | 2083                                     | 0.48                             | 2600                             | 1764                            | 1.20                              |
| 1300          | 1587                                     | 0.42                             | 2467                             | 2200                            | 1.14                              |
| 1350          | 1043                                     | 0.32                             | 2200                             | 3214                            | 0.96                              |

The current density used was the low one of 0.025A/cm², chosen because it was difficult to exceed this current density at the lowest temperatures. As the temperature was increased most of the parameters decreased. This was true of the double layer capacity (col 2), but not the gradient of stage 3; the voltage increment to the start of stage 2 (column 3) and the voltage of oxygen evolution (column 6). The charge increment during stage 2 was different (column 4): it was low at 900°C and at 1000°C, but at a temperature of 1100°C and above was of the same order as the values given in Table IV at the lower current densities. It should be noted from Figure 4(j) that the trace for stage 1 is curved at 1000°C and also that the length of stage 2 is small.

Molybdenum-Soda Lime Silicate Glass

In Figure 5(a) is shown a V/t oscillogram using the sulphate free glass: the upper trace shows the change in the working electrode (anode) voltage with time, and the lower trace is the current track. The point at which the voltage rise starts after the horizontal blanking period is shown, as usual, by the letter "s", and the rise is extremely rapid compared with the rise at a platinum electrode. For example, from Figure 4(c) the time to oxygen evolution at a
current density of 0.083A/cm² is shown as 50msec, and from Table II
the delay time before oxygen evolution at 0.033A/cm² (the nearest
current density recorded for Pt to the 0.042A/cm² value for the Mo)
was found to be 108msec. There is obviously a great difference bet­
ween the electrochemical reactions at the two metals.
This conclusion is confirmed by the photograph of Figure 5(b)
showing the decay times found using the second circuit with the same
glass melt. The remarkable feature of this photograph is the value
of the voltage which is attained during the growth part of the track:
it is roughly 20V and, moreover, remains at approximately the same
size although the current density was varied over the large range of
from 0.017 to 0.083A/cm². These features are not a mistake nor an
error from a single photograph since similar values of the voltage
were found on several other photographs. The final voltage attained is
nearly 20 times greater than that attained at a platinum anode at a
current density of 0.083A/cm² (Figure 4(e)), also using the second
circuit. Two other contrasting features between Mo and Pt are that
the decay at the Mo electrode is almost instantaneous while, with a Pt
electrode discharging into a short circuit, the decay time is approx­
imately 20msec (Figure 4(e)). Additionally, the voltage attained in
the growth part of the trace is hardly increased at all above 20V in
the case of Mo by the increase in current density shown in Figure 5(b)
but an increase in current density increases this voltage considerably
in the case of a Pt electrode (Figure 4(f)).
In Figure 5(c) oscillograms are shown in a glass to which sulph­
ate has been added, Table I, for the working electrode with respect
to a Mo reference electrode and a Pt reference electrode, and also
with the oscilloscope probes connected across the working and aux­
iliary electrodes. The oxygen evolution voltages corresponding to
these three conditions are 1.3, 2.0 and 3.7V, respectively, measured
from the end of the blanking period to the flat part of the plateaux.
Again, the rise to oxygen evolution is extremely rapid, and also the
decay tracks display the same features as those shown by the sulphate
free glass (Figure 5(a,b)).
An unusual feature emerges when the tracks obtained using steady
dc at a current density of 0.042A/cm² and shown in Figure 5(d) are
compared with the pulsating current oscillograms shown in Figure 5(c):
the dc oxygen evolution voltages, while slightly higher than the cor­
responding pulsating current ones, do not differ greatly from them.
This is in marked contrast to the results found with platinum electr­
odes. There the oxygen evolution voltages found using pulsating
current inputs and dc inputs do differ considerably: for example, at
current densities of 0.083 and 0.167A/cm² the voltages measured were
2.9 and 9.3V, respectively, using a dc input, while they were both
1.2V with a pulsating current input at the same current densities.
The oxygen evolution voltages in the sulphate free glass and the
glass to which sulphate has been added have been measured both with
pulsating and direct current inputs, and the results are given in
Table VI. In these measurements no correction for the voltage change
due to the glass resistance has been made. However, by multiplying the

512
glass resistance, measured with the ac bridge at 1000Hz, by the current passing through the cell and subtracting from the measured voltages such a correction may be made (the glass resistance is 80 at 1200°C).

Table VI Effect of Current Density on Oxygen Evolution Voltage in Glasses with and without Sulphate Refiner at 1200°C

| Current Density A/cm² | Oxygen Evolution Voltage(pc) | Oxygen Evolution Voltage(dc) | Oxygen Evolution Voltage(pc) | Oxygen Evolution Voltage(dc) |
|-----------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                       | Sulphate Free V             | Sulphate Free V             | Added Sulphate V            | Added Sulphate V            |
| 0.008                 | 1.00                        | 1.15                        | 0.40                        | 0.52                        |
| 0.013                 | 1.20                        | 1.40                        | 0.56                        | 1.00                        |
| 0.017                 | 1.30                        | 1.50                        | 0.72                        | 1.84                        |
| 0.025                 | 1.60                        | 1.80                        | 0.92                        | 1.16                        |
| 0.033                 | 1.80                        | 2.20                        | 1.30                        | 1.40                        |
| 0.042                 | 2.20                        | 2.40                        | 1.50                        | 1.70                        |
| 0.050                 | 2.60                        | 3.00                        | 2.10                        | 2.80                        |
| 0.067                 | 3.20                        | 3.60                        | 3.00                        | 3.70                        |
| 0.083                 | 4.00                        | 4.40                        | 3.60                        | 4.20                        |
| 0.100                 | 6.50                        | 8.00                        | 4.20                        | 5.00                        |
| 0.133                 | 9.00                        | 11.00                       | 5.40                        | 6.80                        |
| 0.167                 | 11.00                       | 13.00                       | 6.80                        | 10.00                       |

It is clear from the table that the oxygen evolution voltages increase steadily in all cases with increases in current density. Moreover, while the dc values are always slightly higher than the pulsating current values at all current densities, they do not differ greatly from them. A further point is that the values are always lower for the sulphate containing glass than they are for the sulphate free glass, and this is to be expected since the sulphate is a glass refining agent. Another striking feature is that the oxygen evolution voltages attained at the higher current densities are quite large compared with the values which are obtained at platinum electrodes. For example, at a current density of 0.167A/cm² the pulsed and dc values in the sulphate free glass are 11 and 13V, respectively, at the molybdenum electrode; the comparable figures at a platinum electrode at the same current density are only 1.2 and 9.3V, respectively (Table IV).

All of the measurements made against a Mo reference electrode are a few tenths of volts below the values obtained using a Pt reference electrode, and this is not surprising since there is a difference of 0.2-0.3V between the two reference electrodes at 1200°C measured under static conditions, without any current input, before and during the experiments.

The effect of change of temperature on the oscillograms was also examined, and the results are shown in Table VII:
Table VII  Effect of Temperature on Oxygen Evolution Voltage in Glasses with and without Sulphate Refiner at 0.025A/cm²

| Temperature (°C) | Oxygen Evolution Voltage(pc) | Oxygen Evolution Voltage(dc) | Oxygen Evolution Voltage(pc) | Oxygen Evolution Voltage(dc) |
|------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                  | Sulphate Free               | Sulphate Free               | Added Sulphate              | Added Sulphate              |
|                  | V                            | V                           | V                           | V                           |
| 1000             | 4.6                          | 5.0                         | 2.2                         | 2.4                         |
| 1050             | 3.6                          | 4.0                         | 1.6                         | 2.0                         |
| 1100             | 3.0                          | 3.1                         | 1.4                         | 1.6                         |
| 1150             | 2.5                          | 2.9                         | 1.1                         | 1.2                         |
| 1200             | 2.0                          | 2.2                         | 1.1                         | 1.3                         |
| 1250             | 2.0                          | 2.4                         | 1.1                         | 1.3                         |
| 1300             | 1.8                          | 2.4                         | 0.8                         | 0.9                         |

All the voltages for all the glasses decreased with increasing temperature both with pulsating current and with dc inputs. Again the dc values are slightly higher, but comparable in size to those obtained with a pulsating current at all the temperatures considered; the voltages are always higher in the sulphate free glass than it is in the glass to which sulphate has been added.

A striking feature is the size of the voltages in the sulphate free glass at the lower temperatures. These values are much greater than the corresponding values measured at a platinum electrode also in a sulphate free glass (Table V). For example, at 1000°C with a pulsating current input the value at the Pt electrode is 1.37V, while from Table VII the value at a Mo electrode at the same current density of 0.025A/cm² is 4.6V; the value in the glass to which the sulphate has been added is lower at 2.2V.

A series of V/t oscillograms for sodium disilicate, diborate and diphosphate melts were recorded at different current densities and temperatures, and the time to oxygen evolution measured in each case; V/q oscillograms were not examined to the same extent because they were ill-defined in the case of the diborate. The effect of dc polarisation on the various melts was considered in some detail.

Platinum-Sodium Disilicate

In Figure 6(a) is shown an oscillogram at 1200°C and a current density of 0.083A/cm². The track has the same general characteristics as those found in the silicate glass melts: there is an almost linear, rapidly ascending region (stage 1) with a break at 0.4V; this is then followed by a short plateau (stage 2) before another rise (stage 3) to the oxygen evolution plateau (stage 4) at 0.9V.
In Table VIII are given the times to oxygen evolution at the various current densities used.

**Table VIII Effect of Current Density on Time to Oxygen Evolution in Sodium Disilicate at 1200°C**

| Current Density A/cm² | Time to Oxygen Evolution msec | Current Density x Time C/apparent cm² |
|-----------------------|-------------------------------|--------------------------------------|
| 0.017                 | 74                            | 1.26 x 10⁻³                          |
| 0.033                 | 57                            | 1.88 x 10⁻³                          |
| 0.050                 | 27                            | 1.35 x 10⁻³                          |
| 0.067                 | 18                            | 1.21 x 10⁻³                          |
| 0.083                 | 20                            | 1.66 x 10⁻³                          |
| 0.100                 | 15                            | 1.50 x 10⁻³                          |
| 0.133                 | 9                             | 1.20 x 10⁻³                          |
| 0.167                 | 7                             | 1.17 x 10⁻³                          |
| 0.200                 | 5.5                           | 1.10 x 10⁻³                          |
| 0.267                 | 5                             | 1.34 x 10⁻³                          |
| 0.333                 | 3.5                           | 1.17 x 10⁻³                          |

The time to oxygen evolution decreases with increase in current density in the usual way, and the product of the current density and the time to oxygen evolution remains fairly constant. Comparison with Table II where the results for the soda lime silicate glass are given shows that the oxygen evolution times are less for the disilicate than for the silicate glass at the same current densities, and this applies also to the product of the current density and time.

In Table IX the effect of change of temperature is shown:

**Table IX Effect of Temperature on Time to Oxygen Evolution in Sodium Disilicate at a Current Density of 0.05A/cm²**

| Temperature °C | Time to Oxygen Evolution msec | Current Density x Time C/apparent cm² |
|----------------|-------------------------------|--------------------------------------|
| 900            | 33.3                          | 1.67 x 10⁻³                          |
| 1000           | 33.3                          | 1.67 x 10⁻³                          |
| 1100           | 36.0                          | 1.80 x 10⁻³                          |
| 1200           | 36.2                          | 1.81 x 10⁻³                          |
| 1350           | 36.7                          | 1.84 x 10⁻³                          |

The times to oxygen evolution are remarkably constant as is the product of the current density and time. Comparison with the results in Table III for the soda lime silicate glass should be treated with
some caution since these results in silicate glass were measured at the lower current density of 0.025A/cm². However, the times to oxygen evolution in Table IX were still less than those for the silicate glass given in Table III even though the former values were measured at the higher current density of 0.05A/cm². The same applies to the product of current density and time: the values for the disilicate were all lower than those found for the silicate glass.

As did the silicate glass previously studied, the present system recovered rapidly after dc polarisation. This is shown in Figure 6(b) where successive anodic tracks are recorded over a period of about 10sec after a dc polarisation of 30sec at 0.083A/cm²; the final shape and position of the oscilloscope track is similar to that of Figure 6(a). A similar behaviour is recorded at the auxiliary electrode or cathode, shown in Figure 6(c): the track is first displaced towards the lower left hand corner and then recovers to its original position and shape. This cathodic track is shown sloping downwards and away from the anodic track rather than close to it as in Figure 4(d), for clarity, and this was achieved by the simple method of reversing the polarity of the oscilloscope amplifier internally. Next, after dc polarisation both the electrodes recover rapidly within a few seconds in sodium disilicate melts. Similar results were obtained when the polarisation with dc was extended to 5 minutes.

The oscillogram shown in Figure 6(d) is particularly interesting and was made using the second circuit. The cell was polarised initially for 30sec by passing a dc current through the cell of current density 0.083A/cm², and then photographs were rapidly taken of successive, single 100msec pulses discharging into a short circuit. Immediately after the dc polarisation the tracks appear near the upper left hand corner of the photograph, but as time goes on (a few seconds) the tracks move more towards the centre and eventually appear as those in Figure 4(e) when no dc polarisation was used. The interesting thing about Figure 6(d) is that after dc polarisation there is no evidence at all of any of the detail which is present prior to oxygen evolution when the first circuit with pulsating current is used (Figure 6(b)) and the dc polarising conditions are the same. Indeed, the same tracks are completely featureless in Figure 6(d) in this part of the oscillogram and have exactly the same shape as if no dc polarisation was present: there is a steady smooth, curved rise in the voltage with no breaks or direction changes in the graph until oxygen evolution sets in. The decay time of the current is about 20msec into the short circuit and is thus similar to the decay time found in the silicate glass. Figure 6(e) and (f) show the decay tracks using the Pt reference electrode. It is clear from 6(f) that it is the potential of the auxiliary electrode which reverses direction on discharge into a short circuit; and from 6(e) that the discharge is slow into an open circuit.

Platinum-Sodium Diborate

In Figure 7 the oscillograms (a) and (b) are V/t and V/q traces, respectively. Both are featureless compared with the oscillograms in
Figure 6 for the sodium disilicate melt: there are no pronounced breaks in the curves corresponding to oxide film formation.

The effect of change in current density on the time to oxygen evolution is shown in Table X below:

Table X Effect of Current Density on Time to Oxygen Evolution in Sodium Diborate at 1200°C

| Current Density (A/cm²) | Time to Oxygen Evolution (msec) | Current Density x Time (C/apparent cm²) |
|------------------------|--------------------------------|----------------------------------------|
| 0.050                  | 22                             | 1.10 x 10⁻³                          |
| 0.083                  | 20                             | 1.66 x 10⁻³                          |
| 0.100                  | 14                             | 1.40 x 10⁻³                          |
| 0.133                  | 13                             | 1.73 x 10⁻³                          |
| 0.167                  | 10                             | 1.67 x 10⁻³                          |
| 0.267                  | 6                              | 1.60 x 10⁻³                          |
| 0.333                  | 7                              | 2.33 x 10⁻³                          |

The oxygen evolution voltages decrease with increasing current density, as usual, and the product of the current density and time is roughly constant as before.

Figure 7(c) shows the oscillogram at the large current density of 0.200A/cm² and it can be seen that now there are present quite pronounced breaks in the curve. These breaks also occur when the experiment at the lower current density of 0.83A/cm² is repeated after all the experiments at the higher current densities needed to construct Table X had been carried out; this is seen by a comparison of Figures 7(a) and (d). The latter oscillogram shows a pronounced break, while the former does not; the time to oxygen evolution for 7(d) is smaller — about 4msec compared with a value of about 20msec for 7(a); the oxygen evolution is large — about 1.2V — for 7(d) compared with about 0.55V for 7(a). When the charge required for oxygen evolution is calculated from 7(d) it works out at about 0.33 x 10⁻³ C/apparent cm² and this is considerably less than the value of 1.66 x 10⁻³ recorded in Table X for the oscillogram 7(a).

The effect of change in temperature on the time to oxygen evolution at a constant current density is shown in Table XI:

Table XI Effect of Temperature on the Time to Oxygen Evolution in Sodium Diborate at a Current Density of 0.05A/cm²

| Temperature (°C) | Time to Oxygen Evolution (msec) | Current Density x Time (C/apparent cm²) |
|-----------------|--------------------------------|----------------------------------------|
| 900             | 21                             | 1.05 x 10⁻³                          |
| 1000            | 22                             | 1.10 x 10⁻³                          |
| 1100            | 26                             | 1.30 x 10⁻³                          |
| 1200            | 21                             | 1.05 x 10⁻³                          |

With change in temperature at the same current density the time to oxygen evolution and the product are fairly constant as for the disilicate.
An experiment was carried out in which the cell was subjected to anolytic polarisation immediately after which the anodic and cathodic V/t oscillograms were recorded. These are shown in Figure 7(e) and (f), and it can be seen that the anodic oscillograms of 7(e) resemble those in 7(d) and not those in 7(a) which were recorded at the same current density at the start of the series of measurements. The upper track of Fig 7(e), when the voltage was measured across the whole cell, is permanently displaced above the lower track measured across the working and reference electrode: the reason for this is that the cathodic track is distorted by the polarisation as is clear from Figure 7(f). This distortion in the cathodic track remains for some time: the track had not returned to its original position, which is similar in shape to the cathodic track shown in Figure 7(c), 5 min after the end of the dc polarisation.

This prolonged distortion suggests that there is some permanent polarisation occurring at the cathode, and this is borne out by the photograph shown in Figure 7(g). This is a photograph of the cell after the experiment and there is evidently some permanent reaction product round the cathode - that is, at the electrode on the left hand side of the picture. Microscopic and Energy Dispersive Analysis showed this to consist of discrete Pt particles about 0.7 μm in diameter. Such reaction products were never observed after prolonged experiments followed by pulsating current electrolysis in disilicate melts.

**Platinum-Sodium Diphosphate**

While the oscillograms for sodium disilicate and diborate have some similarities the oscillograms for the sodium phosphate melts are completely different. Figure 8(a) shows a V/t oscillogram in this electrolyte at a temperature of 1200°C and a current density of 0.083 A/cm². The difference between this photograph and those for the disilicate (Figure 6(a)) and the diborate (Figure 7(a)) is immediately apparent: there is no linear rise to a short plateau followed by another rise to oxygen evolution; on the contrary the voltage rises slowly over a relatively extended time period and then rises rapidly and directly to oxygen evolution. There are none of the breaks and plateaux on the graphs before oxygen evolution finally occurs which there are with the disilicate and diborate melts (in the later ones, at least).

The times to oxygen evolution are different also. Table XII is a table giving the change in this parameter with change in current density; the values given in the table are the means from several oscillograms.
Table XII  Effect of Current Density on Time to Oxygen Evolution in Sodium Diphosphate at 1200°C

| Current Density A/cm² | Time to Oxygen Evolution msec | Current Density x Time C/apparent cm² |
|-----------------------|-----------------------------|-------------------------------------|
| 0.017                 | 40                          | 0.68 x 10⁻³                         |
| 0.033                 | 24                          | 0.79 x 10⁻³                         |
| 0.067                 | 11                          | 0.73 x 10⁻³                         |
| 0.083                 | 9                           | 0.75 x 10⁻³                         |
| 0.100                 | 5.3                         | 0.53 x 10⁻³                         |
| 0.133                 | 4.7                         | 0.63 x 10⁻³                         |
| 0.167                 | 3.3                         | 0.55 x 10⁻³                         |
| 0.200                 | 2.4                         | 0.48 x 10⁻³                         |
| 0.267                 | 1.8                         | 0.48 x 10⁻³                         |
| 0.333                 | 1.4                         | 0.47 x 10⁻³                         |

It is clear that the time to oxygen evolution decreases with increasing current density as it did in the sodium disilicate and the diborate melts, and also that the product of current density and time does not change greatly although there is a slight drift downwards in value as the current density increases. However, the times to oxygen evolution for the diphosphate at corresponding current densities are much smaller, and the product of current density and time for the diphosphate is about half the size it is for the disilicate and the diborate.

The behaviour with change in temperature is similar in this electrolyte to that in the first two electrolytes studied. Table XIII gives the change in oxygen evolution time with increase in temperature.

Table XIII  Effect of Temperature on Time to Oxygen Evolution in Sodium Diphosphate at a Current Density of 0.05A/cm²

| Temperature °C | Time to Oxygen Evolution msec | Current Density x Time C/apparent cm² |
|---------------|-------------------------------|-------------------------------------|
| 600           | 25                            | 1.25 x 10⁻³                         |
| 700           | 15                            | 0.75 x 10⁻³                         |
| 800           | 9                             | 0.45 x 10⁻³                         |
| 900           | 8.5                           | 0.43 x 10⁻³                         |
| 1000          | 10                            | 0.50 x 10⁻³                         |
| 1100          | 9.5                           | 0.48 x 10⁻³                         |
| 1200          | 10.5                          | 0.53 x 10⁻³                         |
The sodium diphosphate melted at a lower temperature than the disilicate and the diborate, and it was possible to make measurements at 600°C with this electrolyte. Apart from the measurements at the lowest temperatures of 600 and 700°C, the times to oxygen evolution are of the same order and the product of current density and time fairly constant; Figure 8(b) is an oscillogram at 600°C.

The time to oxygen evolution is not the only measurement in the diphosphate melt to give rise to discrepancies compared with the other two melts: the oxygen evolution voltage does this also. In Table XIV are given the oxygen evolution voltages for the three electrolytes at various current densities, measured, of course, against the Pt reference electrode.

Table XIV Comparison of Oxygen Evolution Voltages at Various Current Densities in Sodium Disilicate, Diborate and Diphosphate at 1200°C

| Current Density | Oxygen Evolution Voltage | Oxygen Evolution Voltage | Oxygen Evolution Voltage |
|-----------------|--------------------------|--------------------------|--------------------------|
|                 | Na₂O.2SiO₂ | Na₂O.2B₂O₃ | Na₂O.2P₂O₅ |
| A/cm²           | V          | V          | V          |
| 0.017           | 0.6        | 0.48       | 0.44       |
| 0.033           | 0.8        | 0.46       | 0.48       |
| 0.050           | 0.7        | 0.48       | 0.48       |
| 0.067           | 0.7        | 0.62       | 0.46       |
| 0.083           | 0.9        | 0.76       | 0.48       |
| 0.100           | 0.9        | 0.90       | 0.52       |
| 0.133           | 0.9        | 1.05       | 0.50       |
| 0.167           | 1.0        | 1.05       | 0.52       |
| 0.200           | 1.1        | 1.10       | 0.52       |
| 0.277           | 1.1        | 1.15       | 0.51       |
| 0.333           | 1.1        | 1.20       | 0.50       |

The difference between the three is immediately apparent: while the oxygen evolution voltages for the disilicate and the diborate increase with increasing current density, the values for the diphosphate hardly change and are much smaller than the other two at all current densities and do not increase much with increase in the c.d.

These smaller values of the oxygen evolution voltage persist for diphosphate melts when the temperature is varied. In Table XV the values of the oxygen evolution voltages are given for the three electrolytes from 600 to 1300°C, measured against the Pt reference electrode. The values for the disilicate and diborate melts decrease with increase in temperature as usual, but the oxygen evolution voltages in the diphosphate melts are again much smaller at all temperatures and show only a very slight drift downwards above 800°C.
Table XV Comparison of Oxygen Evolution Voltages at Various Temperatures in Sodium Disilicate, Diborate and Diphosphate at a Current Density of 0.05A/cm²

| Temperature | Oxygen Evolution Voltage | Oxygen Evolution Voltage | Oxygen Evolution Voltage |
|-------------|--------------------------|--------------------------|--------------------------|
| °C          | Na₂₀.²SiO₂               | Na₂₀.²B₂O₃              | Na₂₀.²P₂O₅              |
| 700         | -                        | -                        | 0.62                     |
| 800         | -                        | -                        | 0.54                     |
| 900         | 1.3                      | 1.2                      | 0.52                     |
| 1000        | 1.2                      | 1.0                      | 0.48                     |
| 1100        | 1.04                     | 0.6                      | 0.48                     |
| 1200        | 0.92                     | 0.48                     | 0.44                     |
| 1300        | 0.72                     | -                        | -                        |

The lower values of the oxygen evolution voltages in sodium diphosphate may have something to do with the decay characteristics of platinum electrodes observed in this electrolyte. In Figure 8(e) the decay after a 100msec pulse at 0.083A/cm² is shown into an open circuit, and also into a short circuit, Figure 8(f). Comparison with Figures 4(a) for the soda lime silicate glass melt shows that the decay in the diphosphate is slower than that in the silicate glass melt when discharge is into an open circuit. The most unusual feature, though, is that the voltage reverses polarity when the cell is discharged into a short circuit in the diphosphate melt (Figure 8(f)); when a similar discharge occurs in the soda lime silicate glass melt it is the current which reverses polarity (Figure 4(e)).

Finally the behaviour after dc polarisation was examined in the diphosphate electrolyte. Figure 8(c) is a V/t oscillogram taken 10 minutes after a 30sec dc polarisation at 0.083A/cm², and it can be seen, by comparison with Figure 8(a), that the lower track for the working-reference electrode combination has returned to its original shape and position - though with a lengthening of the period before oxygen evolution - while the track for the working-auxiliary electrode combination has not done so. Again, as in the case of the diborate, this is due to a permanent polarisation of the cathode as is clear from Figure 8(d): the track has the sharp outline characteristic of a polarised cathode compared with the non-polarised cathode track shown in Figure 8(a). When the cell was removed from the furnace it was found that the cathode was surrounded by a layer of reaction product similar to that shown in Figure 7(g) for the diborate melt.

The results of a more detailed dc polarisation experiment on both the easily depolarised disilicate melt and the hard to depol-
arised diphosphate are given in Table XVI:

Table XVI Recovery after DC Polarisation of Cell, Anodic and Cathodic Voltages for Sodium Disilicate, Diborate and Diphosphate melts at 1200°C and 0.083A/cm²

| Polarisation Conditions | Cell Anodic | Cathodic | Polarisation Conditions | Cell Anodic | Cathodic |
|-------------------------|-------------|----------|-------------------------|-------------|----------|
| Na₂0.2SiO₂              | V V         | V V      | Na₂0.2P₂O₅              | V V         | V V      |
| Before                  | 1.94        | 1.04     | Before                  | 1.24        | 0.64     | 0.60     |
| After 5min dc           | 1.08        | 1.04     | After 30sec dc          | 0.68        | 0.64     | 0.04     |
| at 0.083A/cm²           | 1.43        | 1.07     | 2min later              | 0.70        | 0.66     | 0.04     |
| 2min later              | 1.80        | 1.00     | 5min later              | 0.68        | 0.64     | 0.04     |
| 5min later              | 1.84        | 1.00     | 10min later             | 0.74        | 0.64     | 0.10     |

The disilicate was polarised for the longer time of 5min at 0.083 A/cm² dc while the diphosphate was given a shorter polarisation of only 30sec at the same current density. To study the recovery of the electrodes after these polarisations the anodic and cathodic voltages were measured at intervals - the cathodic voltage chosen being that corresponding to the steady, horizontal part of the track. In all cases the cell voltage recorded is the calculated arithmetical sum of these two values.

In the disilicate the cell voltage drops under dc polarisation and this is due to a reduction in the anodic voltage- and a much larger reduction in the cathodic voltage from 0.90 to 0.04V. On removal of the direct current input the anodic voltage recovers almost immediately and the cathodic voltage also in about 2-5min to near its original value (column 4). The behaviour in the diphosphate is completely different. The cathodic voltage drops from 0.6 to 0.04v after only 30sec dc polarisation and has still only recovered to 0.1V 10minutes later (column 8); the anodic voltage hardly changes.

DISCUSSION

The V/t oscillogram of Figure 4(b) shows clearly that the time to oxygen evolution is 2.6msec at a current density of 0.6A/cm² and a temperature of 1350°C. This is greater than the 1msec half cycle time of a 500Hz sine wave and less than the 10msec half cycle time of a 50Hz sine wave. Consequently oxygen gas bubbles do not have time to form at the platinum electrodes during the positive half cycle of a 500Hz electrical input before the polarity is reversed, but they do have time to do so during the positive half cycle of a 50Hz input before its polarity is reversed. Thus the fact, recorded in reference (1), that platinum electrodes do not corrode appreciably at 1350°C and 0.6A/cm² with electrical inputs of frequency 500Hz but do corrode extensively with a similar input at a frequency of 50Hz receives a logical explanation.
Of course, when the temperature and current density are both decreased we would expect the time to oxygen evolution to increase, and that this does actually occur is clear from the oscillogram of Figure 4(c) at the lower temperature of 1200°C and the lower current density of 0.083A/cm²: the time to oxygen evolution, measured from 4(c), is 50msec.

The current density seems to affect the time to oxygen evolution more than the temperature. Thus, from Table II, the time to oxygen evolution decreases twelve-fold - from 122 to 10msec - when the current density is increased from 0.017 to 0.333A/cm²; and it then decreases a further seven-fold - down to 1.4msec - when the current density is further increased to 1.333A/cm². The behaviour with change in temperature is different: apart from the value at the lowest temperature of 900°C, the time to oxygen evolution is remarkably similar at all the other temperatures at the fixed current density of 0.025A/cm². This lack of variation with temperature is unusual in an electrochemical reaction in molten glass.

The really remarkable features of both Tables II and III, however, are the figures shown in columns 3 of both tables which give the products of the current densities and the time to oxygen evolution. Apart from the two values at the lowest and the highest current densities in Table II, these remain constant within the limits of experimental error during a forty-fold change in current density from 0.025 to 1.000A/cm². The same is true when the temperature is changed: from Table III the product of current density and time remains constant within the limits of experimental error as the temperature changes from 900° to 1350°C.

The constancy of the product of current density and time means that the same quantity of electricity is deposited during the electrochemical reaction under all the different conditions of current density and temperature in Tables II and III, and implies that exactly the same electrochemical reaction is occurring under all these conditions. The most likely electrochemical reaction to be occurring in the molten glass is the discharge of non-bridging oxygen ions during pulsating current electrolysis to give oxygen gas.

This unusual phenomenon of constant charge deposition under a wide range of experimental conditions is not confined to pulsating current electrolysis, however, but also occurs with ac sine wave inputs.

Thus Eden(6) electrolysed soda lime silicate glass between platinum electrodes at 1290°C under ac conditions and found that when the current density was high -5A/cm² - then the discolouration of the glass melt started at the high frequency of 2000Hz. The cycle time is then 0.5msec, the charge deposited per cycle is 2.5 × 10⁻⁵ C/apparent cm², and this is the charge required for extensive corrosion to start. In our own work on the corrosion of platinum in molten soda lime silicate under ac conditions described in reference (1), we found that discolouration of the melt started at 250Hz at the lower current density of 0.6A/cm² at a temperature of 1350°C. Then the cycle time was 4msec and the charge necessary for attack to occur was 2.4 × 10⁻³ C/apparent cm². We conclude that this is the quantity of electricity required for extensive attack to occur in molten soda lime silicate glass under
ac conditions of electrolysis.

It is also the amount required for extensive attack to occur in a
different type of glass with a different modifying oxide—high flint
glass with composition 58% SiO₂, 40% PbO, with minor amounts of the
alkali metal oxides. This was shown by Hupfer (7) who electrolysed
this glass at 1100°C with ac between platinum electrodes. He also
found that at lower current densities the frequency had to be correspon­
dingly lower—and thus the cycle time longer—for attack to occur.
Thus at frequencies of 250, 500 and 1000Hz he found that the minimum
current densities for attack and darkening to occur were 0.625, 1.25
and 2.5A/cm², respectively, and in each case these values correspond to
the deposition of a quantity of electricity of 2.5 x 10⁻³ C/apparent cm².
He also noted that the start of this attack coincided with the start of
vigorous evolution of oxygen gas at the electrodes.

It is instructive to compare this figure of 2.5 x 10⁻³ C/apparent
cm² obtained with ac sine wave inputs with the values found in column 3
of Table II for pulsating current inputs. As we have seen these values
are reasonably constant and an average value taken from all the recorded
values in column 3 is 3.3 x 10⁻³ C/apparent cm². Considering the great
difference between the pulsating current conditions and the sine wave
alternating current conditions the agreement between the two figures of
3.3 x 10⁻³ and 2.5 x 10⁻³ C/apparent cm² is good. It could be argued,
of course, that oxygen gas evolution is only possible during the posit­
ive half cycle and that hence the figure of 2.5 x 10⁻³ should be halved.
However, if there is any irreversibility in the process—oxygen gas not
removed during the negative half cycle—then this reversal of current
will not affect the evolution of oxygen gas, and certainly not the cor­
rrosion. Furthermore, the analogy should not be pushed too far: the
quantity, current density x time was called by Hupfer the density of
charge and was used by him purely as a measure of the onset of cor­
rrosion.

We can say that for corrosion in soda lime silicate glass and
flint glass under ac sine wave conditions that 2.5 x 10⁻³ C/apparent cm²
of electricity is the minimum required for corrosion of the platinum to
occur associated with the evolution of oxygen gas; and that 3.3 x 10⁻³
C/apparent cm² is the minimum quantity of electricity for oxygen evolu­
tion to occur under pulsating current conditions. It would thus seem
that under both pulsating current and ac sine wave conditions basically
the same overall electrochemical reaction is occurring—and this is
the discharge of, probably, non-bridging oxygen ions to form oxygen gas
which then causes extensive attack on the hot platinum metal. Whether
or not corrosion actually occurs is determined by the relationship bet­
ween the time to oxygen evolution determined by the pulsating current
method and the half cycle time of the ac input as we described at the
start of this discussion in connection with the corrosion results at
1350°C and a current density of 0.6A/cm².

We consider now some papers of Hickling who worked at room temper­
ature in aqueous solutions, in order to compare his results with our
results at high temperatures. In Figure 9(a) is shown an oscillogram
he obtained with a platinum wire anode in N₂H₂SO₄ at a current density
of 0.01A/cm² (8). We will discuss the details of this photograph later, but the feature which we wish to consider now is the overall quantity of electricity required for oxygen evolution to occur. In the original photograph it was arranged that a displacement of 1mm on the horizontal axis corresponded to 1V. Thus, knowing the value of the series capacitor - 6μF - and the fact that Figure 9(a) is a two times reduction of the original photograph, it is possible to calculate the amount of electrical charge deposited from the start of the track to the onset of oxygen evolution at the second, upper horizontal plateau. This works out at 3.06 x 10⁻³ C/apparent cm² and, astonishingly, is almost equal to the mean value of 3.3 x 10⁻³ C/apparent cm² found from Table II for molten soda lime silicate glass at 1200°C. Furthermore the values for the charge required for oxygen evolution in neutral and alkaline solution (N-NaOH) work out at 3.06 x 10⁻³ and 3.24 x 10⁻³ C/apparent cm², respectively. This close agreement between the two sets of results in aqueous solution at room temperature and in molten glass at 1200°C strongly suggests that the electrochemical reaction occurring in the two systems is basically the same: the discharge of monovalent hydroxyl ions or of bivalent, non-bridging oxygen ions to give diatomic oxygen gas.

This agreement between the results in aqueous solutions and in molten glass is not confined to platinum but occurs also for other noble metals such as gold (9), and also the more reactive metals: nickel (10), cobalt (11) and silver (12), that Hickling and his co-workers studied. In Table XVII we have calculated the quantity of electricity required for the onset of oxygen evolution at these different metals - Pt, Au, Ni, Co, Ag and also Cu (13) in various electrolytes of different pH. For the more reactive metals only alkaline NaOH solutions have been considered - apart, that is, from various buffer solutions which will be discussed later in connection with the diborate and diphosphate results we found in molten glass. We have quoted only alkaline solutions because Hickling found that in acid solutions all the metals, apart from platinum and gold, simply dissolved at their respective dissolution potentials. A further complication is that some of the metals used - Co, Ag and Cu - were used in plated form and the accessible or true surface area was many times greater than the geometric, apparent surface area (see Table XVII, column 5). For platinum and gold wire electrodes, Hickling took the ratio of the true to the apparent surface area to be 2, and we have used this value as our standard. We have reduced the experimentally determined values of the charge for oxygen evolution recorded at the higher true surface areas to this common ratio of 2 even though the actual ratio of the true to the apparent surface area for a particular metal may be much larger. In this way we compare the different metals on the same basis, and it is these reduced values of the quantity of electricity required for oxygen evolution which are given in column 4 of Table XVII.

From an examination of the results in N-NaOH for all the metals, it is clear that the quantity of electricity required for oxygen evolution is of the same order for all these metals except copper when it is much larger. Hickling and Taylor (13) concluded that a 6 - 7 molecule thick
poorly protective layer of CuO formed on the copper electrode during electrolysis and then dissolved in the N-NaOH. Support for this came from the experimentally observed facts that the oscillograms were greatly dependent on changes in current density, temperature and concentration of NaOH, unlike the other metals: Table XVII shows that as the concentration of NaOH is decreased to 0.3N the charge necessary for oxygen evolution decreases to a figure of $3.65 \times 10^{-3}$ C/apparent cm$^2$ which is near the usual figure found for the other metals in N-NaOH. The figures shown in Table XVII for gold electrodes are less than those for platinum because, for gold, the initial part of the oscillogram due to adsorbed hydrogen is absent.

This remarkable similarity in the charge required for oxygen evolution to start strongly suggests that the process occurring at all the metals is basically the same—in alkaline solutions, at least (but modified by the high solubility of the CuO in the case of copper)—and consists in all cases of the formation of an oxide film on the metal just prior to the start of oxygen gas evolution.

When the alkalinity of the electrolyte is decreased by using buffer solutions and, ultimately, acid solutions, the value of the charge required for oxygen evolution usually decreases for the more reactive metals; however, for the noble metals—platinum and gold—this does not occur, and the value of the charge remains the same in alkaline, neutral and acid solutions. Thus, narrowing down the discussion to the noble metals, and platinum in particular, we conclude that the quantity of electricity required for oxygen evolution to occur is the same for platinum electrodes in aqueous solutions (alkaline, neutral and acidic) and in molten glass at 1200°C. Since the overall electrochemical reactions are the same, we consider that the detailed steps of these reactions must have great similarities in aqueous solutions and in molten glass, and we now compare these detailed steps for platinum electrodes in aqueous solutions and in molten glass.

The two oscillograms which we choose to compare these two systems are the V/q oscillograms for Pt in N-H$_2$SO$_4$ at 18°C of Figure 9(a) and that for Pt in molten glass at 1200°C shown in Figure 4(g). Hickling divided the track of Figure 9(a) into three stages before oxygen evolution started. Stage 1 consisted of the initial, curved part of the trace below about 0.25V, and he ascribed this to the ionisation of free and adsorbed hydrogen following Butler and Armstrong (14). Stage 2, the steeply ascending part between 0.25 and 0.87V, he ascribed to the charging of an electrical double layer of capacity 200μF/apparent cm$^2$. Stage 3 is the most important part of the track and started at a potential of 0.87V. Grube (15) had found that the reversible potential of platinous oxide (PtO) against platinum in 2N-sulphuric acid was 0.9V and this, by applying the usual equation for the variation of potential with hydrogen ion concentration, gave a static potential of 0.88V in 1N-H$_2$SO$_4$. Hickling thus concluded that the break recorded in the oscillogram at 0.87V corresponded with the onset of PtO formation on the electrode. This was also true for neutral and alkaline solutions (Table XVII) because the potentials of the breaks in the oscillograms of 0.50 and 0.06V, respectively, recorded for these solutions corresponded closely.
with the static oxide potentials of 0.49V and 0.07V calculated from the results of Grube in these electrolytes.

The lengths of the tracks from this break in the curve up to the start of oxygen evolution are extremely important. The quantity of electricity calculated from this is found to be 1000μC/apparent cm² for all the solutions - acid, neutral and alkaline - and this is sufficient for the liberation of approximately 3.1 x 10¹³atoms of oxygen. Taking the specific gravity of platinum to be 21.4, the diameter of the platinum atom is calculated to be approximately 2.5 x 10⁻¹⁰cm, and hence there should be about 1.6 x 10¹⁵atoms of metal per square cm at the platinum surface. Hickling took the ratio of the true to the apparent surface area to be 2, and this was based on the work of Bowden and Rideal (16) who compared the capacities at different metal electrodes with that at a mercury electrode in the same solution for which the true surface area was assumed equal to the apparent surface area. Using this true surface area, the number of platinum atoms on this accessible or true surface area of 3.2 x 10¹⁵is almost equal to the number of atoms of oxygen - 3.1 x 10¹⁵liberated by electrolysis, and thus stage 3 was taken to correspond to the formation of a monomolecular layer of platinum oxide, PtO₂, on the surface of the electrode.

We now ask how these conclusions compare with the results we have found at platinum electrodes in molten glass. In Figure 4(g) there is, of course, no part of the curve corresponding to the ionisation of hydrogen stage in aqueous solutions, but we may still divide the track into three stages before oxygen evolution starts. First, there is stage 1, a rapidly ascending region which extends to a voltage of about 0.45V when there is a break in the curve which corresponds to the onset of stage 2. During this stage the potential grows more slowly and the track extends to a considerable length across the photograph. Eventually, however, there is another break in the curve when the track starts to ascend rapidly again; this is denoted as stage 3 and immediately precedes oxygen evolution which starts at about 1.2V.

We ascribe stage 1 (which corresponds to Hickling's stage 2) to the formation of an electrical double layer as in the aqueous case. By measuring the x-axis displacement and recalling that the series capacitor used is 100μF, the charge accumulated in this stage is calculated to be 400μC and, by dividing by the voltage rise of 0.45V to the start of stage 2, the capacity of the double layer is calculated to be 889pF or 2963pF/apparent cm². This is much greater than the 200-300pF/apparent cm² found by Hickling (8) but is not surprising in view of the difference between the dielectric constants of the two systems (100 and 6μF/sed).

Table IV shows that the value of the double layer capacity remains fairly constant at current densities below 0.333A/cm², but that after this it drops. This is not surprising in view of Figure 4(i) at the high current density of 0.333A/cm²: the track is curved in the stage 1 region and hence the double layer capacity concept is of doubtful validity at and above this current density. This is also a feature of Figure 4(j) and may explain, to some extent, why the double layer capacities at the lower temperatures of 900° and 1000°C are different from the rest at higher temperatures in Table V.
The start of stage 2 occurs at a voltage of 0.45V where the track in Figure 4(g) changes direction, and we now ask what this means. We may calculate the voltage required for the formation of the oxide PtO₂ from the thermodynamic work of Alcock and Hooper (17) on the formation of this oxide. They measured the vapour pressure of PtO₂ at several temperatures between 1100°C and 1550°C and expressed their results by the free energy equation:

$$\Delta G^0 = 39270 \pm 340 - T(0.93 \pm 0.21) \text{ cal/mole.} \tag{1}$$

At a temperature of 1200°C (1473°K) $\Delta G^0$ lies between 38,540 and 37,251 cal/mole. and using the relationship:

$$\Delta G^0 = nE^0F, \tag{2}$$

the voltage at which the reaction:

$$Pt + O_2 = PtO_2 \tag{3}$$

would be expected to occur lies between 0.42 and 0.40V. These results have been confirmed by Schafer and Tebben (18): at 1208°C they measured a free energy of formation of PtO₂ of 37,777 cal/mole. corresponding to a potential of 0.41V. Since the voltage at which the break in the curve occurs is 0.45V on the oscillogram, the agreement between prediction and experiment is good, and this supports the conclusions from the work of Alcock and Hooper. These calculations thus strongly suggest that the oxide of platinum which forms at the break in the oscillogram track is the oxide PtO₂.

From Table IV it is clear that the voltage at the start of stage 2 increases with current density away from the reversible, thermodynamic value of Alcock and Hooper. This is to be expected as the system will depart more and more from the reversible state as the current density is increased. Table V shows, on the other hand, that this voltage decreases with increase in temperature and this not unexpected. However, the equation [1] of Alcock and Hooper predicts that the voltage of PtO₂ formation should vary but slightly with increase in temperature: at 1100°C the mean calculated value is 0.403V, and at 1350°C the value is 0.40V.

We now enquire how much of the oxide, PtO₂ is formed on the electrode surface during stage 2. From the measurements from Figure 4(g) we found that the charge accumulated during stage 2 was 2000μC/apparent cm². Using a value of the Faraday of 96,500 C/gm equivalent and Avogadro's Number of 6.023 x 10²³ atoms/gm atom, we calculate that this is sufficient for the liberation of 6.2 x 10¹⁵ atoms of oxygen. Taking the specific gravity of platinum to be 21.4 and its atomic weight as 195.23 we calculate, using a solid sphere model, that the diameter of the platinum atom is approximately 2.5 x 10⁻⁸ cm and therefore there should be about 1.6 x 10¹⁵ atoms of metal per geometric cm² of surface. Taking the ratio of the true or accessible surface area to the apparent or geometric surface area to be 2, after Hickling, we have that there are 3.2 x 10¹⁵ atoms of platinum per true cm². Thus for every platinum atom on the surface there are two oxygen atoms and stage 2 thus cor-
respond to the formation of a monomolecular layer of PtO$_2$ on the platinum surface. This is in contrast to the case in aqueous solution where a monomolecular layer of the lower oxide, PtO, forms. However, since both oxides are monomolecular layers, the times to oxygen evolution will be the same in each case, and this explains why the figures in column 3 of Table II for the high temperature system and column 4 of Table XVII for the aqueous system N-NaOH are of the same order. The formation of these oxide films - PtO$_2$ in the molten glass case, and PtO in the aqueous case - explains why the onset of oxygen evolution is delayed during electrolysis; and the occurrence of this delay also explains why it is that corrosion of the Pt by oxygen gas occurs with a 50Hz ac input but not with a 500Hz input (see reference (1) and also Figure 4(b).

The position is not quite as clear cut as it looks, however, in the light of some later work by El Wakkad and Emara (19) on the platinum electrode in solutions of varying pH. In order to determine more accurately what is happening during the various stages of the overall process, they passed constant currents of very low current density - typically 17μA/apparent cm$^2$ - using freshly plated platinised platinum electrodes of geometrical surface area 1.8cm$^2$. However they, in this work found a ratio of true to apparent surface area of 180 and so their current density was the extremely low one of 0.094μA/cm$^2$. They used a direct potentiometric method to measure the voltage and they found that at the low current densities they were using they took over an hour to plot the full graph.

One of their graphs for 0.1N-H$_2$SO$_4$ is shown in Figure 9(b), curve A. It can be seen from this figure that its general features agree with the oscillograms of Hickling shown in Figure 9(a). However, in Figure 9(b) there are two breaks in the curve before oxygen evolution occurs and not one, as in Figure 9(a) at a much higher current density, and using the oscillographic method. These two breaks occurred at potentials of 0.82 and 1.05V, respectively, and these values agree well with the static equilibrium potentials of 0.82V and 1.1V calculated from the work of Grube (15) for the system Pt-PtO and Latimer (20) for the system PtO$_2$-PtO$_2$. It appears, therefore, that PtO is not the only oxide which can form at the platinum electrode during pulsating current electrolysis in aqueous solutions, but that PtO$_2$ can form also as in the molten glass case.

This oxide is unstable, however: El Wakkad and Emara studied the decay of polarisation after oxygen evolution had been attained and the curve they obtained is shown as curve B in Figure 9(b). This shows that when the circuit is broken the potential drops to a break in the curve at just under 1.0V where the unstable PtO$_2$ decomposes to PtO.

The potential then levels out at about 0.8V which is the potential of the couple Pt-PtO, and then this oxide persists. When oxygen evolution has occurred and the anodically polarised anode is made cathodic then the curve C of Figure 9(b) is obtained. This shows that now there is only one break in the curve starting at about 0.7V and corresponding to the reduction of PtO. This reduction is over in a short time and then the potential drops rapidly to zero. These results
show clearly that a reverse current polarisation—such as that which occurs with the pulsating current method—is necessary to strip all trace of the oxide film from the surface, and that it is not sufficient to rely only on the natural discharge for this to occur. The same two oxides were also found in neutral and alkaline solutions—at different electrode potentials, of course.

In addition to this work, El Wakkad and Emara also used the oscilloscopic method of Hickling at Pt electrodes in 0.1N-H₂SO₄, using Pt wire electrodes of apparent area 0.1cm² and a current density of 100μA/apparent cm². They found that the formation of PtO occurred at a potential of 0.8V, and that of PtO₂ at 1.07V.

There is some doubt about which process is occurring in stage 3. One possibility is that higher oxides of platinum form. This was considered by Schneider and Esch (21) by measuring the vapour pressure of platinum oxides formed by passing a mixture of argon and oxygen over platinum metal heated to 1200°C. They found that PtO₃ formed between oxygen pressures of 311 and 810mm Hg and PtO₄ at pressures greater than 890mm. The measured free energies of formation of the two oxides were 48,609 and 60,095 cal/mole, respectively, and these correspond to voltages of 0.53 and 0.65V. As stage 3 starts at a voltage of about 0.7V from Figure 4(g) this suggests that the formation of PtO during stage 3 is a possibility.

This conclusion is not supported by what is occurring during stage 3 however, with respect to the quantity of electricity passed. The charge accumulated during this stage is 667μC/apparent cm², corresponding to the liberation of 2.0 x 10¹⁵ atoms of oxygen per apparent cm² or 1.0 x 10¹⁵ atoms of oxygen per true cm². Since there are 1.6 x 10¹⁵ atoms/cm² at the platinum surface, this can only add one atom, at most, to the PtO₂ to give PtO₃. Since the thermodynamic calculations do not favour the formation of this oxide, but rather the formation of PtO₄, we are forced back to the conclusion that another, higher oxide is not formed during stage 3 but that this stage corresponds to the formation of an additional monatomic layer on top of the PtO₂ film already present on the electrode. In addition, the curve is steep during this part of the track and resembles the rapidly rising part due to the charging of the double layer as is apparent from an examination of Figure 4(g). Not only this, but from Table IV, column 5, the gradient of stage 3 is one of the most stable parameters found and this contrasts with the variability of the charge increment shown in column 4 which decreases at the higher current densities, and which is associated with the growth of the PtO₂ film. Thus the evidence given above would seem to suggest that, on balance, additional oxides do not form during stage 3 of Figure 4(g) for a platinum electrode in molten silicate glass, but that rather the formation of an additional double layer of oxygen ions on the PtO₂ film already on the electrode is favoured prior to oxygen evolution.

It is seen from an examination of Table IV that the gradient of stage 3, measured in μC/V, is among the most stable parameters measured as the current density changes, and this true also of the oxygen evolution voltages given in column 6 of Table IV. Below a current density
of 0.25A/cm² these hardly change at all, but there is a small, progressive increase after this at high current densities; no linear plots of $V$ against $\ln I$ or $I$ could be obtained from this data, however.

In an experiment on reproducibility using 22 different oscillograms at the same current density of 0.083A/cm², it was found (1) that the oxygen evolution voltage had the smallest coefficient of variation of 2.3% of any of the parameters measured; and the 95% Confidence Interval for this measurement was (1.19, 1.21V). This constancy of the oxygen evolution voltage under pulsating current conditions contrasts strongly with its variability with dc inputs. For example, with a pulsating current of 0.083A/cm² the oxygen evolution voltage was 1.20V, while with dc it was 2.9V; with a pulsating current of 0.167A/cm² the voltage was again 1.20V, while with dc it was 9.3V. There thus seems to be a large amount of polarisation at the electrode, using dc — probably due to the accumulation of oxygen gas round the electrode due to the high viscosity of the melt. This does not occur to the same extent during the pulsating current electrolysis because of the shortness of the oxygen evolution plateaux, and the fact that the electrode reactions are reversed and the electrode returned to its original condition every cycle. Thus the pulsating current method gives much more realistic and reliable values for the oxygen evolution potentials than does the dc method.

The work we have done indicates that the platinum electrode is a reliable reference electrode. When the three tracks on the photograph of Figure 4(d) were discussed it was noted that the sum of the Y-coordinates for the trace of the working against the auxiliary electrode was equal to the sums of the values for the tracks of working against reference electrode and reference electrode against auxiliary electrode. This is to be expected, of course, but the important observation from these traces is that there is no curvature in opposite senses in the two latter tracks, particularly towards the end of the pulse when oxygen evolution is occurring. If such an effect had been observed it would have meant that the potential of the platinum wire electrode was changing. This is because if it does change at all in whichever direction, positive or negative, it must change in the opposite senses with respect to the working and the auxiliary electrodes. The fact that no such curvature is observed means that the potential of the platinum electrode remains constant during the electrolysis.

This constancy of the electrode potential of the platinum electrode means that it may be used as a reference electrode, and indeed many authors have so used it — for example, Plumat and his collaborators (22-24) in molten glass, and Janz, Cohen and Segusa (25) in molten carbonates. If the potential of the platinum electrode is taken at all temperatures to be zero then the voltages of the working and auxiliary electrodes are their potentials on the platinum electrode scale. A drawback to this is that the variation of the potential of the platinum electrode with concentration of oxygen ion is not known in molten salt solutions. Its great virtues are its simplicity and robustness compared with reference electrodes based on yttria/zirconia or calcia/zirconia. Furthermore there are drawbacks to using these reference electrodes because Tran and Bungs (26-28) concluded from an extensive
investigation that the Y₂O₃/ZrO₂ reference electrode was the only one that could be used in molten glass between 1000°C and 1350°C since the CaO/ZrO₂ electrode corroded rapidly and the MgO/ZrO₂ cubic structure was unstable below 1400°C.

One of the most important features of the pulsating current method is that the oscilloscope tracks are very stable: they may be recorded hours or days after the start of electrolysis with the same result. They also recover rapidly and permanently after dc polarisation. Figure 4(h) shows successive tracks recorded after a 30sec dc polarisation. Starting from the upper, left-hand corner of the photograph, the curves move down slowly across the screen towards the centre until they occupy a central position which corresponds with the track before the dc polarisation and where they remain indefinitely.

These curves deserve further consideration. The first couple of curves photographed after the dc polarisation have very little detail in them, but appear rather like the single pulse tracks shown in Figure 4(e) and (f). As time goes on breaks begin to appear in the tracks, and they grow larger and less steep. Since the dc polarisation liberates large amounts of oxygen at the electrode it seems not unreasonable to suppose that for the first few traces the large reverse current is removing this oxygen either in the form of oxygen ions or adsorbed oxygen ions, or even PtO₂ if, indeed, it forms on the electrode. Consequently there is not much reverse charge left to remove the monomolecular layer of PtO₂ which is present on the electrode and so it is only partially removed. When the next positive pulse is applied most of the PtO₂ oxide film is still on the electrode, and so the length of stage 2 - during which the PtO₂ film is formed - is short. Eventually, as the excess oxygen gas disappears, the reverse charge strips away more and more of the oxide film and so, during the next positive pulse, more and more PtO₂ oxide film is formed: thus the stage 2 part of the track lengthens. Ultimately the track settles down to an equilibrium condition in which the monomolecular layer of PtO₂ is formed and stripped completely away every cycle. It should be noted that the gradient of stage 2 changes during recovery from the dc polarisation - it becomes less steep - while the gradient of stage 3 remains constant. This is a further reason for distinguishing between what happens during stage 2 and 3: PtO₂ oxide film formation during stage 2 and adsorption of oxygen ions and not formation of PtO₃ during stage 3. It is also worth noting that Hickling (8) using Pt electrodes in N₂-H₂SO₄ found a similar increase in the slope of his stage 3 - due to PtO formation - after an initial dc polarisation, and that the original trace was only restored if the electrode was swung all the way between oxygen and hydrogen evolution; if the amplitude control (the series capacitor size) was adjusted so that this condition was not met and the swing of the electrode potential was restricted then the gradient of the trace could not be reduced to its original value before polarisation. This is strong evidence that with the pulsating current method under normal working conditions the electrode is brought back to its original condition before electrolysis every cycle.
This type of mechanism may explain, to some extent, why it is that the charge increment in stage 2 decreases with current density as shown in column 4 of Table IV. It may be that at these higher current densities there is an excess of oxygen gas formed at the electrode and a large part of the reverse current charge is used up in re-ionising this rather than stripping the PtO$_2$ oxide film away. Consequently on the subsequent cycles some of the oxide film remains on the electrode and hence the charge increment during stage 2 is less than before. It is interesting to note again that the charge increment per volt during stage 3, when oxygen adsorption is considered to occur and not further oxide film formation, remains fairly constant as the current density is increased to its highest value. It is interesting to note also that when the current density is constant, as it is in Table V, then the charge increment is also of the same order, at least for the higher temperatures above 1000°C. At the lower temperature of 1000°C stage 2 is preceded by a very curved stage 1 and the double layer concept is, consequently, of doubtful validity here.

We have seen from Figure 4(h) that when the Pt electrode is anodically polarised with dc the first few following pulsating current tracks have no breaks in them but that after this, in subsequent tracks, breaks occur. No such breaks in the tracks have ever been observed in single pulse experiments with the second circuit - and the tracks of Figure 4(e) and (f) are typical of this behaviour. It was noted in the Results section that the voltage attained in the single pulse experiment of Figure 4(e) was 0.9V at a current density of 0.083A/cm$^2$ and a temperature of 1200°C after allowing 0.2V off for the glass resistance; on the other hand, a voltage of 1.5V was recorded for the pulsating current experiment shown in Figure 4(c) at the same current density and temperature. It was tentatively assumed that in the single pulse experiment oxygen evolution was never attained. However, it may be that the cause of this discrepancy is different. It may be due to the fact that there is no PtO$_2$ oxide film formation in the single pulse experiment because it is already present there on the electrode before the electrolysis starts: only in the pulsating current electrolysis is the oxide film stripped away during the high reverse current pulse and so only during the anodic pulse of this electrolysis can an oxide film form. Thus the fact that there are always breaks present in the pulsating current tracks, but none ever present in the single pulse tracks receives a logical explanation. This would also explain the difference in oxygen evolution voltage of 0.9V and 1.5V for the single and the pulsating current electrolyses: if the voltage rise of about 0.5V shown in Figure 4(c), and due to the formation of the PtO$_2$ film, is discounted then the oxygen evolution voltage is reduced to about 1.0V, which is similar to the value found in the single pulse experiment.

We summarise this part of the work as follows: In the pulsating current electrolysis at platinum electrodes in molten silicate glass, an average quantity of electricity of $3.3 \times 10^{-3}$ C/apparent cm$^2$ is required for the commencement of oxygen evolution under the various conditions of current density and temperature which we have described. This value is of the same order as that required at room temperature for
the evolution of oxygen to occur in acidic, neutral and alkaline aqueous solutions at platinum electrodes, and at other various metals: Au, Ni, Co and Ag in N-NaOH solution.

As a result of this there is a delay before oxygen evolution starts and the cause of this is, first, the charging of an electrical double layer followed by the formation of a monomolecular oxide film which covers the electrode — of composition PtO₂ in the molten glass, and PtO in the aqueous solutions. This film is completely stripped away by the large reverse current, except at the highest currents used, and this is the characteristic feature of the technique, distinguishing it from the other methods, such as the single pulse method, where this stripping does not occur. The oscilloscopic tracks obtained using this method are remarkably stable and recover rapidly after dc polarisation.

**Platinum-Sodium Disilicate**

A comparison of Tables VIII and II shows that the quantity of electricity required for oxygen evolution is much less at platinum electrodes in molten sodium disilicate than in the soda lime silicate glass at all the current densities studied. A comparison of the V/q oscillograms for the disilicate melt from Figure 6(a) and the silicate glass from Figure 4(a) shows why this is so: the length of stage 2 during which the oxide film is forming over the electrode is much less for the sodium disilicate electrolyte than for the silicate glass one. The charge accumulated during stage 2 for the sodium disilicate is only 750μC/apparent cm² from Figure 6(a) compared with a charge of 2000μC/apparent cm² for the silicate glass melt from Figure 4(a), and we might thus conclude that the surface of the platinum is only 38% covered with PtO₂ in the disilicate melt. However, since the concentration of Na₂O is much higher in the disilicate, at 34%, than it is at 11% in the silicate glass, the concentration of free, non-bridging oxygen ions must also be much higher in the disilicate. It is thus difficult to see how a smaller amount of oxide film forms on the platinum electrode in the disilicate than in the silicate glass electrolyte. A much more likely explanation is one similar to the one we used to explain the oscillograms for the platinum electrodes in the silicate glass after dc polarisation: that is, that in the sodium disilicate electrolyte, since there are more free, non-bridging oxygen ions present, there is more oxygen present at the electrode, and that some of the reverse current is used up in reducing the oxygen molecules to oxygen ions and desorbing them so that there is less charge available for stripping away the PtO₂ film. Consequently there is some PtO₂ film remaining on the electrode after the reverse pulse has ended, and during the next positive half cycle only a part of the PtO₂ has to be replaced. Thus the charge devoted to doing this is correspondingly less.

This conclusion is certainly supported by the oscillogram in Figure 6(b), which shows successive tracks after 30sec dc polarisation. Just as for the disilicate glass electrolysis in Figure 4(h), the first few tracks after the dc polarisation are almost featureless with very short plateaux due to the oxide film formation; and as the effects of
the dc polarisation wear off the length of the plateaux increase until, finally, the original shape before dc polarisation is restored. We explained this previously, in the case of the silicate glass electrolyte, as being due to the progressive removal of the excess oxygen gas round the electrode, which was generated from the dc polarisation, and the same explanation will apply in this case for the disilicate. Finally, when the stable position of the track has been reached, the length of the plateau will still be less than in the silicate glass case: there is then still some excess oxygen on the electrode in the disilicate electrolyte due to the high concentration of free, non-bridging oxygen ions present in the melt, and part of the reverse current is used to remove this – hence there is less charge to remove the PtO₂ film and thus it is not completely removed.

We could never completely remove the oxide film plateaux from the pulsating current tracks by using a large amount of dc polarisation; but on the other hand, we never succeeded in introducing any breaks and plateaux into the curves we obtained using single anodic pulses. This is clear from Figure 6(d) which shows several successive single shots using the second circuit after 30sec dc polarisation: in none of the tracks is there the slightest suggestion of any breaks due to oxide film formation. We conclude that this is because, in the single pulse experiments, there is already an oxide film present on the platinum electrode before the start of electrolysis and that only in the pulsating current method is the oxide film stripped off from the electrode during the large, negative reverse current pulse. The pulsating current method is thus unique in providing an electrode in the same reproducible state at the start of every anodic pulse.

The oscillogram of Figure 6(c) shows the successive tracks after a 30sec dc polarisation at the auxiliary electrode and should be compared with the anodic tracks at the working electrode shown in Figure 6(b). The recovery at the auxiliary electrode after the dc polarisation is rapid as it is at the working electrode, but the values in Figure XVI show that the auxiliary electrode recovers more slowly than the working electrode. In the light of this experiment the single pulse oscillograms shown in Figure 6(e) and (f) are very interesting. Figure 6(f) shows that the voltage of the auxiliary electrode reverses polarity during the discharge into a short circuit and this suggests that there is some product on the electrode which is decaying. One possibility is that there is a slight amount of alloying occurring at this electrode due to the large reverse current - Figure 17(b) of reference (1) shows that such alloying of silicon with platinum can take place during prolonged ac electrolysis with a superimposed dc bias.

This result may go some way towards explaining the single pulse oscillogram of Figure 4(e). There we saw that when the cell is discharged into a short circuit the current reverses its direction. We thought originally that this was due to the decay of the PtO₂ oxide film on the working electrode, but in the light of Figure 6(f) – and assuming that the same thing happens in silicate glass as in the disilicate electrolyte – we conclude that this reverse current is caused by the decay of a product at the auxiliary electrode and not at the
working electrode, and that this current is driven through the oxide film on the working electrode which, being thin, will have a low resistance. Thus the conclusion which we reached in the last paragraph but one that the PtO₂ oxide film remains on the platinum electrode after a single pulse is supported by this fresh evidence.

Some of the other parameters for disilicate melts differ considerably from those for the silicate glass, while others do not. When they do so the difference can usually be explained as due to the differing concentrations of Na₂O in the two electrolytes and, hence, the differing amounts of free oxygen ions present.

This probably explains why the double layer capacity of stage 1 calculated from Figure 6(a) is so low at 1245μF/apparent cm², and comparable to the value of 1038 μC/apparent cm²/V for the gradient of stage 3 in the same figure. Since there is a large amount of PtO₂ film remaining on the electrode after the reverse pulse, the process in stage 1 during the next positive half cycle may be predominantly adsorption of oxygen ions on this film as in stage 3.

Again, the oxygen evolution voltage of 0.9V is low compared with the 1.2V recorded for the silicate glass melt (Figure 4(a)), and this is true at all the current densities considered, as a comparison of Tables IV and XIV for the silicate glass and the disilicate will show. This again is not unexpected at the higher concentration of free non-bridging oxygen ions in the disilicate electrolyte because the reversible electrode potential is decreased by increase in oxygen ion concentration. Denoting the reversible electrode potentials in the silicate glass and the disilicate as \( E_1 \) and \( E_2 \), respectively, and the standard electrode potential of the oxygen electrode as \( E^\circ \) we have, from the Nernst Equation, that

\[
E_1 - E_2 = E^\circ - \frac{RT}{nF} \ln [O^\circ_1] - E^\circ + \frac{RT}{nF} \ln [O^\circ_2]
\]

[4]

\[
E_1 - E_2 = -\frac{RT}{nF} \ln \frac{[O^\circ_1]}{[O^\circ_2]}
\]

[5]

We have used the European Convention for the sign of the electrode potential because these particular results are more clearly explained in this way since the sign of the standard electrode potential of the oxygen electrode is positive on this convention. If we make the very crude approximation that the concentration of free, non-bridging oxygen ions is proportional to the concentration of Na₂O we have

\[
E_1 - E_2 = -0.029 \log \frac{(11)}{(34)}
\]

[6]

or

\[
E_1 - E_2 = -0.029 \log (0.3235)
\]

\[
= 0.014V,
\]

and so

\[
E_2 = E_1 - 0.014.
\]

[7]

Thus the reversible electrode potential in the silicate glass is reduced by increasing the concentration of free, non-bridging oxygen ions.
to the higher value in the disilicate melt, and thus we might expect the potential for the irreversible evolution of oxygen to be reduced also. The voltage for oxygen evolution in the disilicate is reduced by increasing the temperature as shown in Figure XV, and this behaviour is similar to that found for the silicate glass electrolyte in Table V; the values in the disilicate are always less than the corresponding ones in the silicate glass at all temperatures, however.

The parameter which does remain constant in both the electrolytes is the potential at the start of stage 2: this is 0.45V in the silicate glass melt compared with 0.44V in the disilicate, and this similarity is not surprising since both represent the start of PtO2 formation on the electrode.

We summarize this part of the work as follows: The pulsating current electrolysis in the disilicate electrolyte is similar to that in the silicate glass melt in that a roughly constant amount of electricity has to be supplied to obtain oxygen evolution at all the current densities and temperatures considered. The difference is that the quantity of electricity required is less in the disilicate than it is in the silicate glass composition: an average of 1.3 x 10^-3 C/apparent cm^2 is sufficient for oxygen evolution in the disilicate, but an average of 3.3 x 10^-3 C/apparent cm^2 is necessary for the silicate glass. This is because the PtO2 oxide film is only partially stripped away from the electrode during the reverse current pulses, and this itself is due to the higher concentration of oxygen at the electrode at the end of the positive half cycles due to the higher concentration of free, non-bridging oxygen ions in the disilicate melt.

The recovery after dc polarisation is rapid in the disilicate melt as it is in the silicate glass electrolyte, and a comparison of the pulsating current and single pulse electrolyses shows that, once again, only in the pulsating current method is there any stripping away of the PtO2 oxide film.

Platinum-Sodium Diphosphate

We consider the diphosphate melt before the diborate one because it is the one which differs the most from the disilicate and silicate glass electrolytes which are similar to one another. The long initial, curved region in the oscilloscope tracks for diphosphate shown in Figure 8 (a) and (b) at temperatures of 1200° and 600°C are best explained as being due to the dissolution of the electrode in the melt to give platinum phosphate and the deposition of a phosphate salt film on the electrode prior to oxygen evolution. We could never induce the breaks and plateaux indicating oxide formation which we observed so often in silicate melts, and this was true even though we changed the current density 20-fold and the temperature from 600° to 1350°C.

The formation of a platinum phosphate film is certainly possible chemically since there is evidence in the literature that platinum can dissolve to a greater extent in phosphate glass melts than in silicate or borate glass ones. Thus, Rindone and Rhoades (29) added platinum as PtCl4 solution to sodium silicate, borate and phosphate glass composi-
tions containing 1 mole of the modifying oxide to 4 moles of the glass former in each case. When the glass had been formed on fusing they found that in the phosphate glass the platinum at a concentration of 0.1% gave a yellow colouration indicating ionic dissolution, but a grey colour, indicating colloid formation, at concentrations of 0.01% and 0.001% in the silicate glass and the borate glass, respectively. This evidence supports the view that during the anodic pulse platinum dissolves in the phosphate melt and then precipitates on the electrode as a salt film.

That such a salt film does indeed form on the electrode is strongly suggested by the decay curves shown in Figure 8(f) for discharge into a short circuit. This shows clearly that the voltage of the anodic working electrode reverses direction during the discharge in the diphosphate melt, and it differs from Figure 4(e) for the silicate glass in this respect in that, for that oscillogram, the anodic voltage did not reverse its voltage but the current did. The fact that the polarity of the working electrode changes sign during the discharge suggests that there is some product present on the electrode which decays during the discharge, and that this is more substantial than the oxide film present on the electrode in the disilicate since there was no reversal of polarity of the working electrode in that electrolyte after a single pulse (Figure 6(f)). Close examination of Figure 8(f) shows that there are actually two tracks appearing on the photograph after the positive single pulse has ended, and the second track must correspond to the decay of the voltage on the auxiliary electrode without reversal of polarity.

The presence of a phosphate film on the electrode could explain the results shown in Tables XII to XV. Thus the quantity of electricity required for oxygen evolution in the diphosphate electrolyte is less than that for the disilicate at the various current densities studied, as comparison of Tables XII and VIII will show. In the diphosphate case there is no oxide film formation to delay the onset of oxygen evolution; the same thing is true at different temperatures, as an examination of Tables XIII and IX will show.

Another feature of oxygen evolution voltages in diphosphate melts is that they remain at the same low value as the current density and temperature are varied, and this is in contrast to the values in the silicate melts where the oxygen evolution voltages are not only larger but also change appreciably with change in current density and temperature (see Tables XIV and XV). This may easily be explained if there is a thick phosphate salt film on the electrode of large surface area: such a film would decrease the true current density enormously and would result in a lower oxygen evolution voltage under all conditions. This film cannot be of a very permanent and protective character, however because Table XVI shows that after dc polarisation the voltage of the working electrode reduces rapidly to its value before dc polarisation. It is the polarisation of the auxiliary electrode shown in column 8 of Table XVI which is the cause of the long term change in the track with the oscilloscope across the cell from working to auxiliary electrode shown in Figure 8(c); the relatively permanent polarisation
at the auxiliary electrode is shown in Figure 8(d). We have seen that alloying may explain some of the results at the auxiliary electrode or cathode during the reverse pulse in the disilicate electrolyte and, to anticipate the borate results, alloying at the cathode occurs to a considerable extent there. It may well be that something similar may happen at the cathode in the diphosphate and explain the prolonged polarisation which, from Table XVI, is there some considerable time after the polarisation.

The work of Hickling and Spice on the polarisation of nickel anodes in aqueous solutions (10) throws further light on what is occurring in molten phosphates. In Figure 10(a) and (b) are shown the tracks obtained in N-NaOH and 0.2M-KH$_2$PO$_4$ + 0.2M-Na$_2$HPO$_4$ buffer solution of pH 6.8 at room temperature. The oscillogram for N-NaOH shows an initial very rapidly ascending region followed by a break at 0.55V indicating the start of Ni$_2$O$_3$ formation, which forms a film slightly thicker than 1 molecule thick before oxygen evolution starts at about 0.85V. The oscillogram for the phosphate buffer is completely different, however: the voltage rises directly to oxygen evolution without any break due to oxide film formation and with only a small curvature; the cathodic track is similarly featureless showing only a small peak before hydrogen evolution. Figure 10(c) shows the result of an experiment to find out what is happening in the early stages of the electrolysis. First the nickel electrode was polarised cathodically at 0.01A/cm$^2$ for about 3 min to free the surface from any existing film; then the pulsating current was switched on and the first few tracks photographed. They are shown as numbers 1 to 4 in Figure 10(c). In 1 a process, probably of simple dissolution of nickel phosphate, occurs at a potential of −0.1V; this is repeated in 2, but is followed by a rapid rise in voltage; in 3 the voltage rises to oxygen evolution almost immediately and 4 is the normal form of the track shown in 10(a), and this remains unchanged thereafter. Hickling and Spice concluded that, on being made anodic, the nickel dissolves to form an insoluble phosphate which coats the electrode forming a protective and conducting film which subsequently remains stable. This film could, however, be removed by continuous dc cathodic treatment for after such treatment the sequence of tracks could again be observed.

While this is a perfectly logical explanation for the results found by these authors it is not sufficient to explain our results as exemplified in Figure 8(a) and (b). The anodic tracks there are permanent and stable and the track of working electrode against reference electrode may be considered to be intermediate between tracks 2 and 3 of Figure 10(c) of Hickling and Spice which we have just discussed. This would suggest that the anodic track of Figure 8(a) corresponds to the initial dissolution of platinum to form platinum phosphate followed by the formation of a partially stable and semi-protective film. It is possible that on reversal of the current the film is completely stripped away, but it is more probable that it is only partially stripped off from the electrode. This is because Hickling and Spice calculated that more than 10,000µC/apparent cm$^2$ had been used in the formation of the stable phosphate salt film obtained in their experiment and this
is equivalent to the dissolution of about $30 \times 10^{15}$ nickel atoms in the bivalent state, or rather more than 4 atomic layers from the electrode surface. We did not repeat this experiment, but the quantity of electricity corresponding to the initial, curved part of the track in Figure 8(a) is about $147\mu\text{C/apparent cm}^2$ and is thus less than the $2000\mu\text{C/apparent cm}^2$ required to form a monomolecular layer of PtO$_2$ on a clean, oxide-free platinum electrode in molten silicate glass electrolyte. If the phosphate salt film is formed and completely removed every cycle then the electrode is never completely covered by the salt film. But the salt film must completely cover the electrode because it protects the surface completely from the formation of any oxide film, and its large surface area reduces the oxygen evolution voltage as shown in Table XIV. A more likely explanation of what is occurring at the electrode is as follows: We assume that the first few tracks at the start of the experiment are similar to numbers 1 and 2 found by Hickling and Spice, and that the central track, for the working/reference electrode combination, which we see in Figure 8(a), is the third and stable position for the subsequent tracks. Then the quantity of electricity used to form the salt film works out at $7250\mu\text{C/apparent cm}^2$, and this is equivalent to the dissolution of $23 \times 10^{15}$ platinum atoms in the divalent state or rather more than 7 atomic layers from the electrode surface. Rindone and Rhoades (29) are of the opinion that there are some Pt$^{4+}$ ions in the glass even though the PtCl$_4$ they added decomposed to PtCl$_2$. If this were so then the number of platinum atoms dissolving would be halved as well as the number of atomic layers. This would give a mean value for the number of atomic layers as just over 5; it is probably safe to say that the platinum phosphate salt film, when fully formed is between 5 and 7 atomic layers thick. Once this salt film is established it is protective in the sense that it completely inhibits the formation of an oxide film on the electrode - we never saw any evidence for oxide film formation in any of our experiments in diphosphate melts under any conditions; and it must also be of large surface area to explain the low values of the oxygen evolution potentials found in Table XIV. However, our track is unlike the static trace of Hickling and Spice shown in Figure 10(b) which corresponds with a completely stable salt film. The fact that there is evidence of metal dissolution before salt film formation for every positive half cycle in Figure 8(a) - the first, slowly curving part of the track - must mean that during the negative half cycle some of the film dissolves away - helped, of course, by the large, negative reverse current. Thus the salt film is partially removed during every reverse cycle and then built up again during the next positive half cycle; but it never completely disappears from the electrode.

We summarize the results found in this section as follows: In sodium diphosphate electrolyte, in contrast to sodium disilicate, there is no oxide film formation occurring under any of the conditions we have considered. However, there is present on the electrode a protective phosphate salt film, several atomic layers thick and of large surface area, which is partially removed and replaced during every cycle of the pulsating current.
Platinum-Sodium Diborate

The behaviour of a platinum electrode in sodium diborate electrolyte is intermediate between its behaviour in sodium disilicate and in sodium diphosphate.

Thus in the V/t and V/q oscillograms shown in Figure 7 there is very little detail in 7(a), the V/t oscillogram, prior to oxygen evolution and almost none in the V/q oscillogram of 7(b). At the higher current density of 0.200A/cm², however, there is a well marked break in the curve followed by a plateau - shown in Figure 7(c) - and this corresponds to the formation of an oxide film on the surface of the electrode. The really interesting photograph in this series, however, is Figure 7(d) which is a repeat oscillogram of 7(a) at the same current density of 0.083A/cm², but taken after all the other measurements at the higher current densities had been made. It is clear from the tracks that now, in contrast to Figure 7(a) and (b), there is a well defined break in the curve followed by a plateau before the final rapid ascent to oxygen evolution. These features show that there is an oxide film forming on the electrode surface during cycling.

The length of this plateau is small - it is finished in about 2msec - and this corresponds to a quantity of electricity of only 167μC/apparent cm². If we assume, as in the case of the silicate glass melt, that a charge of about 2000μC/apparent cm² represents full coverage of the electrode surface with a monomolecular layer of PtO₂, then we must conclude that the electrode is only 8.5% covered in the diborate melt and this seems unlikely. There is always the possibility, of course, that the oxide is only partially stripped away during the reverse cycle as in the sodium disilicate melt, and the charge we are seeing on the oscillogram is merely the charge necessary to cover the rest of the partially stripped surface.

Hickling and Spice (10) found a similar shortening of the time to oxygen evolution at nickel anodes in N-NaOH when the electrolyses were carried out in 0.1N-Na₂B₄O₇ solutions. Thus the length of the tracks before oxygen evolution in Figure 10(a) in N-NaOH was reduced, on the original photograph, from about 51mm to 30mm when the NaOH was replaced by 0.1N-Na₂B₄O₇ solution; this corresponded with a reduction in the charge required for oxygen evolution of from 5400μC/apparent cm² to 3180μC/apparent cm². Hickling and Spice did more than this: they cathodically polarised an electrode for 3min with dc at 0.01A/cm² in the 0.1N-Na₂B₄O₇ solution before examining the first few pulsating current tracks. The results are shown in Figure 10(d) and it can be seen that the first track marked "1", shows no detail, but that the second track 2 shows a well defined break due to oxide film formation. The length of this break in the track 2 before oxygen evolution is about 25mm on the original photograph and corresponds with a quantity of electricity of about 2600μC/apparent cm², which is somewhat less than the 3180μC/apparent cm² found under steady state, continuous running conditions. They had shown previously that 4500μC/apparent cm² was sufficient to form a monomolecular layer of Ni₂O₃ on the nickel electrode in N-NaOH solution and the comparable value of 2500μC/apparent cm² for the borate corresponds...
to a 0.55 surface coverage. Thus track 1 corresponds to the formation of a salt film on the surface of the electrode which is only partially protective since in one cycle it gives way to an oxide film partially covering the surface, which is cyclically formed and removed during the pulsating current electrolysis.

This cannot be the explanation of what is occurring in the molten sodium diborate, however, because the tracks in Figure 7(a) and (b), which we ascribe to the formation and removal of a salt film, are repetitive and the oscillograms are stable; only when high currents of 0.200A/apparent cm² are applied does the formation of oxide films start and continues thereafter at the lower current densities. We ascribe the tracks in Figure 7(a) and (b) to the formation of a salt film on the surface of the platinum electrode. From Table X, the quantity of electricity required for oxygen evolution is 1660μC/apparent cm² at a current density of 0.083A/apparent cm² and we calculate that this amount of charge corresponds to the dissolution of 5.2 X 10¹³ atoms in the bivalent state or a salt film of just over ½ molecules thick, using a specific gravity of 21.4. When the high current density of 0.200A/apparent cm² is applied the film ruptures and is then replaced by an oxide film forming and reforming as shown in Figure 7(c). The quantity of electricity corresponding to the break in the curve is only 300μC/apparent cm², and this represents only 15% coverage of the electrode surface with the oxide film. We note from the initial part of Figure 7(c) that the track is curved and, as are the tracks for diphosphate, this indicates dissolution of metal. This dissolution may be one reason for the rupture of the salt film at the higher current densities, but another may be the formation of platinum-boron alloys on the electrode during the large negative pulses of the reverse half cycle. It is well known that boron alloys easily with platinum at high temperatures (30) and this may be the reason for the extensive attack shown in Figure 7(g) at the cathode; if a similar slight attack takes place at the working electrode during high current density pulses then this could sensitize the surface and perhaps allow the formation of oxide films there. The tracks in Figure 7(d) are almost identical with those formed at the last and highest current density of 0.333A/apparent cm² used, in that the plateau due to oxide film formation is so short — about 2msec — as is the time to oxygen evolution — almost 4msec. It could be that on the passage of the highest current density there is a slight amount of alloying of the working electrode which sensitizes the surface and allows a stable oxide film to form over most of it; then the cyclic formation and removal of the oxide film occurs which only corresponds to a coverage of the surface of about 8.5%. If a part-boron oxide does form on the electrode surface then it will be stable since the strength of the boron oxygen bond is greater than that of the silicon-oxide one: the values are 119 and 106kcal, respectively, according to Sun (31).

Support for the idea outlined above comes from the photograph of Figure 7(e) which was taken immediately after 5 min dc polarisation at 0.083A/apparent cm². Although there must be a large amount of oxygen round the electrode the track of working against reference electrode is almost identical with that in 7(d) showing that the over-riding factor...
determining the shape of the curve is the effect of the past application of a very high current density and not the dc polarisation; if there had been partial stripping of the film at the electrode then we would have expected dc polarisation to have had a very great effect on the shape of the pulsating current tracks as in the case of the silicate glass and the disilicate melts. There is polarisation at the auxiliary electrode as shown in Figure 7(f) and this displaces the track of the working electrode against the auxiliary electrode upwards in Figure 7(e).

The behaviour of platinum in sodium diborate electrolyte is complicated, but we summarize the results in this section as follows: At the lower current densities protective salt films form on the platinum electrodes and there is no evidence of oxide film formation. At the higher current densities, however, breakdown of the salt film occurs as well as, possibly, some alloying of boron with the platinum of the working electrode. When this occurs a stable oxide film forms on the electrode surface, only a small amount of which is periodically stripped away and reformed during the pulsating current cycle.

Molybdenum-Soda Lime Silicate Glass

If the reaction at a platinum electrode is characterised in silicate, borate and phosphate melts by the formation of thin oxide or salt films then, for a molybdenum electrode, nearly all the evidence points to the conclusion that its behaviour is dominated by the presence on the electrode of a more or less permanent, thick oxide film.

Certainly the metal oxidises very easily in air or oxygen: Stroud (32) describes molybdenum electrodes used in glass melting furnaces some parts of which must be protected from oxidation by an inert gas atmosphere at temperatures as low as 500°C. At higher temperatures of 1300°C and above Bartlett (33) found that cylindrical molybdenum rods decreased in diameter by the large amounts of 0.36 and 2mm per hr at pressures of 0.1 and 1atm, respectively, and this corresponded to reaction rates of $1 \times 10^{-4}$ and $6 \times 10^{-3}$ cm/sec at the two pressures. The attack on the metal by free, non-bridging oxygen ions in melts may be even greater than this since Rosner and Allendorf (34) maintain that the attack of molybdenum by oxygen ions can exceed that due to gas molecules by two orders of magnitude. Certainly both the extent and the velocity of the reaction of molybdenum with oxygen is much greater than that of platinum. Thus Gulbransen, Andrew and Brassart (35) found a value of $-104$ kcal/mole for the standard free energy at 1200°C of the reaction:

$$2 \text{Mo} + \frac{3}{2} \text{O}_2 = 2 \text{MoO}_3$$

and this should be compared with the positive value of $+38$ kcal/mole found by Alcock and Hooper (17) for the oxidation of Pt to PtO$_2$. Again Gulbransen and his co-workers found that the linear reaction rate for the oxidation of molybdenum in oxygen was 530mg/cm$^2$/hr and this is enormously greater than the value of 0.23mg/cm$^2$/hr found for the oxidation of platinum in oxygen by Fryberg and Petrus (36), again at 1200°C.
Oxide films form on molybdenum electrodes in glass melts with and without the passage of electrical current. Thus, Boffe, Delzant and Plumat (37) concluded that the film they observed on Mo rods heated for 65 hr in sulphur-free soda lime silicate glass at temperatures from 1000°C to 1300°C were oxides of molybdenum; they also found a concentration of MoO₃ in the glass of up to 3.78 wt%. The most extensive attack on molybdenum electrodes occurs, however, when refining agents such as SO₃, Sb₂O₃ or As₂O₃ are added to the glass. Thus, Hierl, Hanke and Scholze (38) found that Mo electrodes corroded about twice as rapidly in soda lime silicate glass melts containing Sb₂O₃ at 1250° - 1350°C than they did without any added refining agent; and when the Sb₂O₃ was replaced by added sulphate the extent of the reaction increased a further three times. They identified reduced antimony on the electrode using EDAX and they found a Mo-S compound on the electrode using the electron microprobe. This work was carried out using an applied ac current of 50 Hz which caused anodic oxidation during the positive half cycle according to the authors; and the extent of the reaction increased with current density.

The glasses in which the greatest reaction occurs, however, are the lead silicate glasses. Matej, Truhlavora and Rycl (39) electrolysed a glass of composition 21% PbO, 65% SiO₂ and 14% K₂O between heated Mo electrodes at current densities from 0 to 3 A/cm² at 1200°C and 1400°C. They found reduced Pb on the electrodes on top of the oxides of molybdenum at both temperatures, and with and without current; there was also liquid lead on the bottom of the crucible from the electrode. The composition of the layer of product on the electrode was found to be 60% Mo, 11% Pb and 4% K; the corrosion increased with increasing current density. These results are not surprising since we calculate from the linear free energy table of Coughlin (40) that the standard free energy of the reaction:

\[
\text{Mo} + 3 \text{PbO} = \text{MoO}_3 + 3 \text{Pb} \]  \hspace{1cm} \text{[9]}

is \(-66.4 \text{kcal/mole of MoO}_3\) at 1200°C.

In the light of the results which we have discussed it seems probable that during pulse electrolysis there is present on the molybdenum electrode a thick film of oxide which determines the type of oscillogram obtained. Thus the voltage rise shown in Figure 5(b), found using the single pulse circuit, is no less than the extremely high value of 22V at a current density of 0.042 A/apparent cm² in the sulphate-free glass. This is an extremely large voltage change to encounter compared with the value of 2.2V found from the pulsating current oscillogram of Figure 5(a) at the same current density. It is not due to an observational error because similar voltages were found from several other, different oscillograms. Furthermore, this latter value of 2.2V from the pulsating current circuit is itself greater than the more usual value lying between 1.18 and 1.2V found for a platinum anode at current densities of 0.033 and 0.083 A/apparent cm² (Table IV). We measured the resistance of the glass in the cell at a frequency of 1000 Hz using platinum electrodes and found it to be 80. Thus we assign a voltage drop due to the
resistance of the glass of $8 \times 0.042 \times 0.6 = 0.20V$. If we take the actual voltage required for oxygen evolution to be, say, the $1.2V$ needed to evolve this gas at a platinum electrode having on its surface the low resistance monomolecular layer of PtO$_2$ then the most we can ascribe to glass resistance and oxygen gas evolution is $1.4V$. Subtracting this from the $22V$ we have measured in Figure 5(b), we are left with $20.6V$ to account for. Even if we subtract the $2.2V$ for oxygen evolution found in Figure 5(a) for the pulsating current electrolysis using the first circuit, we are still left with $19.8V$. It seems to the author that the only way these large voltage drops can be satisfactorily explained is that they are due to the presence on the electrode of a high resistance molybdenum oxide layer, probably MoO$_3$ (35). If this is so we may calculate its resistance by dividing the current of $0.042 \times 0.6 = 0.025A$ passing through the cell and, doing this, we obtain resistance values of 824 and 792Ω corresponding to voltages of 20.6 and 19.8V, respectively. This is a very high resistance for such a small area (0.6cm$^2$) film and it would have been useful to have calculated its thickness knowing its resistivity. Unfortunately, however, the most probable oxide occurring at these temperatures is MoO$_2$ according to Gulbransen, Andrew and Brassart (35) and this has a melting point at 795°C and sublimes at 1155°C (41). Above 800°C, indeed, the above authors found that the oxide MoO$_3$ volatilised as fast as it was formed if the oxygen pressure was 1atm. That is not to say, though, that the gas phase reaction they studied is exactly comparable with the electrolytic system we are concerned with. Indeed, although Gulbransen and his co-workers are of the confirmed opinion that MoO$_3$ is the oxide forming throughout their investigation, other authors give thermochemical data such as the standard free energy up to a temperature of 1727°C (see Coughlin (40) and King, Weller and Christensen (42)) for the oxide MoO$_2$. It is possible that a film of MoO$_3$ can form on the electrode surface and remain there at the high temperatures we are using since the oxide is encapsulated in the glass and is dissimilar to a system of a flowing stream of oxygen gas at 1atm pressure. That some thick film is present on the Mo electrode even before electrolysis is shown by a measurement of the glass resistance we made at 1200°C and 1000Hz using the molybdenum electrodes. We found a resistance of 130Ω which is very much greater than the 8Ω we found with platinum electrodes under the same conditions. There is certainly a thick film on the Mo electrode after electrolysis: Figure 2 and 3 of reference (5) shows such a film on the electrode. The photograph there is a 2/3 reduction of the original and the bars on the original are each 8μm long. Consequently the average thickness of the film is about 40μm. The film was shown to be an oxide film by wave length dispersive analysis. It is probable then that the large voltage rise got with the single pulse experiment (Figure 5(b)) is simply due to the voltage drop across the large resistance of a very thick film of oxide already present on the electrode before electrolysis begins. This explains the shape of the tracks: the voltage rises and decays extremely rapidly and there are none of the slowly ascending tracks and slow decays associated with platinum electrodes in silicate glass or sodium disilicate, or even diphosphate.
We turn now to a consideration of the pulsating current tracks in Figure 5(a). In the upper track showing the voltage of the working electrode there are none of the delays characteristic of the polarisation at a platinum electrode and due to the formation and decay of a thin oxide film; rather the voltage jumps almost immediately from its rest value to oxygen evolution as, indeed, it does for the single pulse experiment shown in Figure 5(b). Since the voltage jump of about 2.2V for the pulsating current is much less than the 22V found with the single pulse oscillogram, we are forced to the conclusion that any oxide film with the pulsating current electrolysis must be very much thinner. If we subtract 1.4V as before to allow for the glass resistance and the voltage needed for oxygen evolution at a metal such as platinum where there is only a thin, low resistance film present, then we are left with 0.8V to account for, and this corresponds to a film with a resistance of only about 300. At first sight these two figures of 300 and 8240 for the resistances of the two films for a pulsating current and a single pulse, respectively, and at the same current densities also, may seem to be contradictory. However, it should be borne in mind that there is a very high current spike passed through the cell in the reverse direction in the pulsating current electrolyses and this will have the effect of reducing the thickness of the oxide in the electrode.

The thickness of the film on the molybdenum electrode must increase with increasing current density because, as column 2 of Table VI shows, the oxygen evolution voltage increases with increasing current density. Thus, at current densities of 0.083 and 0.167A(apparent cm²) the oxygen evolution voltages are 4 and 11V, respectively, and subtracting 0.4V and 0.8V (since the oxygen evolution voltage at a platinum electrode is still 1.2V from Table IV), we have for the film resistance, values of 48 and 900 for the two current densities. These resistances correspond to films which are thicker than the 300 one at a current density of 0.042A/apparent cm², but they are much thinner than the film with resistance 8240 from the single pulse experiment shown in Figure 5(b)—also at a current density of 0.042A/cm². We might still explain this difference as being due to the reduction of the oxide thickness on the Mo electrode by the reverse current. But if we do this, how are we to explain the figures in column 3 of Table VI which show that the dc oxygen evolution voltages are only slightly higher at all the current densities than the pulsating current ones? There is no reverse current operating in this case and so why are the two sets of voltages—and, by implication, the resistances of the films—of roughly the same size? It can only be that the over-riding factor which is controlling the oxygen evolution voltage and the film thickness is not the reverse current pulse but the actual evolution of oxygen gas on the electrode, with the consequent sublimation of some of the volatile MoO₃. It does not seem possible that the negative reverse current pulse can remove films of the thickness we envisage by itself, alone—certainly not if the films are of MoO₃ which, according to Coughlin (40) is a solid at 1727°C. The presence of MoO₃ on the electrode, which may voltilise in the gas stream and does so according to Gulbransen, Andrew and Brassart (35), seems to be the only way to explain the results we have obtained.
We conclude that the mechanism of the reactions occurring at the anodic molybdenum working electrode are as follows: Initially, due to the high negative free energy of the reaction, there is formed on the molybdenum electrode a thick film of the oxide $\text{MoO}_3$ not free to move from the surface of the electrode because of the constraints imposed by the presence of the surrounding molten glass. When a single pulse is applied the resistance of this film determines the shape and size of the oscilloscopic tracks and, since only a single pulse is applied, the film is not altered or disturbed. When an anodic dc current is flowing, however, the thickness of the film is reduced to a value depending on the current density by the extensive evolution of oxygen gas at the electrode, which allows some of the $\text{MoO}_3$ to volatilise away in the gas stream. The same thing occurs when the pulsating current is applied, but helped to a small extent by the current reversal during the negative half cycles.

Oscillograms obtained with a pulsating current input in the glass with added sulphate are shown in Figure 5(c). They are of the same basic shape as those found for sulphate free glass 5(a) and (b) and, as is clear from Figure 5(d), the oxygen evolution voltages are similarly only less than the dc values by a small amount. Potentials in the two photographs are given with reference to a Pt reference electrode and also a Mo reference electrode, and it can be seen that there is a difference between the two: this is due to the 0.2-0.3V recorded under static, reversible conditions using a digital voltmeter for the difference between a Pt and Mo electrode.

The oxygen evolution voltages for glass containing added sulphate are less than those for sulphate free glass under all the different conditions of current density and temperature which we examined and which are shown in Tables VI and VII. It would be surprising if it were otherwise since sulphate is added to molten glass as a refining agent to aid the removal of oxygen gas bubbles by itself providing a source of $\text{SO}_2$ and $\text{O}_2$ gas. It can be seen by comparing columns 4 and 5 in these tables that the dc values are again slightly higher than the pulsating current values as they were in the sulphate free glass. The two sets of values are so similar, indeed, that we may ascribed the same mechanism of film formation and stability to both - with the added complication in the case of the sulphate containing glass, of course, that the gas $\text{SO}_2$ is involved in the removal of the $\text{MoO}_3$ film as well as oxygen gas.

While it is considered that the oxide is the main component of the film surrounding the anodic working electrode, nevertheless sulphides can also form on the molybdenum electrodes. Most of the authors we have quoted with respect to molybdenum and, notably Hierl, Hanke and Scholze (38); Matej (43); Boffe, Delzant and Plumat (37) find sulphides present on their electrodes in one form or another as well as oxides. Certainly the formation of sulphides is thermodynamically possible for Stubbles and Richardson (44) found the standard free energy of the reaction:

$$\frac{4}{3}\text{Mo} + \text{S}_2 = \frac{2}{3}\text{Mo}_2\text{S}_3$$  \[10\]
to be -32kcal/mole of Mo2S3 at 1200°C, using the linear free energy equation:

$$\Delta G^0 = -85,700 + 36.4T.$$  \[11\]

**SUMMARY**

The pulsating current technique which we have described allows the measurement of many of the parameters involved in the electrochemical reactions occurring at polarising electrodes: the time to oxygen evolution (crucial as the deciding factor in whether a platinum electrode corrodes or not with an alternating current input); the quantity of electricity required for oxygen evolution; the capacity of the electrical double layer; the type and thickness of any oxide or salt film formed on the electrode; the reproducible values of the oxygen evolution potential, free from the polarising effects which are almost inseparable from dc measurements made in high temperature viscous melts.

The quantity of electricity required for oxygen evolution is usually constant for any one particular electrode/electrolyte combination and is independent of changes in current density and temperature within the limits of experimental error. The details of the reactions which occur before oxygen gas evolution then depend upon both the electrode material and the electrolyte. For platinum electrodes in molten silicate glass there is the complete removal of a monomolecular layer of the oxide PtO2 every cycle followed by its fresh replacement; for sodium disilicate the replacement and removal are partial. For molten sodium diphosphate there is the partial removal and re-formation of a protective salt film on the electrode surface every cycle; for sodium diborate there is the initial formation of a partially protective salt film followed by breakdown and oxide film formation at the higher current densities. When the electrode material is changed to the reactive molybdenum the electrode kinetics are dominated by the permanent presence on the electrode of a thick oxide film.

The technique thus enables a detailed picture of the fast electrochemical reactions which are occurring to be built up, and in this the method is far superior to single pulse techniques. Its unique advantage over such methods is that it returns the electrode to its initial condition at the end of every cycle either completely stripped of oxide and salt film or in an equilibrium, partially stripped condition. It is the author’s opinion that this pulsating current technique has been greatly neglected by electrochemists in comparison with the enduring interest shown in the other method which Hickling pioneered: the electronic potentiostat (45-48). Whenever basic data on the electrochemical reactions occurring at polarising electrodes is required which is free from bulk diffusion effects the method has a great deal to recommend it. It is ideally suited to the study of corrosion reaction mechanisms, but it may also be used to study cathodic processes such as electrodeposition; and it can be used with porous as well as bulk electrodes.
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Figure 1 Pulsating Current Circuit

Figure 2 Single Pulse Circuit
Figure 3 High Temperature Electrolysis Cell
Pt Electrode-Soda Lime Silicate Glass

(a) 100 Ω load; 0.167 A/cm²
Y₁=5V/d; Y₂=0.02V/d
T=10μsec/d
MP3...E
MP1...E

(b) 1350°C
0.600 A/cm²; 100μF
Y₁=1V/d; Y₂=0.01V/d
T=2μsec/d
W(MP4)...E
A(MP1)...E

(c) 1200°C
0.083 A/cm²; 100μF
Y₁=0.5V/d; Y₂=0.01V/d
T=10μsec/d
W(MP4)...E
A(MP1)...E

(d) 1200°C
0.083 A/cm²; 100μF
Y₁=0.5V/d
T=10μsec/d
W...A (1)
W...R (2)
R...A (3)
Figure 4 (cont)

Pt Electrode-Soda Lime Silicate Glass

(e) 1200°C
0.083 A/cm²
Y₁=0.2V/d; Y₂=0.01V/d
T=20msec/d
W(MP4)...E
A(MP1)...E
Cell discharged into 10MQ, 10Q and 0Q

(f) 1200°C
0.033, 0.083, 0.167, 0.333 A/cm²
Y₁=0.5V/d
T=20msec/d
W(MP4)...E
Cell discharged into 0Ω
Figure 4 (cont)
Pt Electrode-Soda Lime Silicate Glass
V/q Oscillograms

(i) 1200°C
0.333A/cm²; 100µF
Y=0.5V/d
X=2V/d
W(MP4)...R(MP2)

(j) 1000°C
0.025A/cm²; 100µF
Y=0.2V/d
X=2V/d
W(MP4)...R(MP2)
Successive shots after 30sec polarisation (dc)
Figure 5

Mo Electrode-Soda Lime Silicate Glass

(a) 1200°C
0.042 A/cm²; 50 μF
Y1 = 2 V/d; Y2 = 0.01 V/d
T = 2 msec/d
W(MP4)...E
A(MP1)...E
Sulphate Free

(b) 1200°C
0.017, 0.042, 0.083 A/cm²
Y1 = 10 V/d
T = 20 msec/d
W(MP4)...E
Into 10 MO and 00
Sulphate Free

(c) 1200°C
0.042 A/cm²; 50 μF
Y1 = Y2 = Y3 = 1 V/d
T = 2 msec/d
W(MP4)...R(MP2)Mo
W(MP4)...R(MP2)Pt
W(MP4)...E
Added Sulphate

(d) 1200°C
0.042 A/cm²; 50 μF
Y1 = 1 V/d
T = 2 msec/d
W(MP4)...R(MP2)Mo
W(MP4)...R(MP2)Pt
W(MP4)...E
DC Input
Added Sulphate
Pt Electrode-Sodium Disilicate

(a) 1200°C
0.083A/cm²; 50µF
Y=0.2V/d
T=5msec/d
W(MP4)...R(MP2)
A(MP1)...R(MP2)
Anodic/Cathodic

(b) 1200°C
0.083A/cm²; 50µF
Y=0.2V/d
T=5msec/d
W(MP4)...R(MP2)
Successive shots after 30sec dc at 0.083A/cm²
Anodic

(c) 1200°C
0.083A/cm²; 50µF
Y=0.2V/d
T=5msec/d
A(MP1)...R(MP2)
Successive shots after 30sec dc at 0.083A/cm²
Cathodic

(d) 1200°C
0.083A/cm²
Y1=0.5V/d; Y2=0.01V/d
T=20msec/d
W(MP4)...E
A(MP1)...E
Successive shots after 30sec dc at 0.083A/cm²
Cell discharged into 0Ω
Figure 6 (cont)
Pt Electrode-Sodium Disilicate

(e) 1200°C
0.083A/cm²
Y1=Y2=0.2V/d
T=20msec/d
W(MP4)...R(MP2)
A(MP1)...R(MP2)
Cell discharged into 10MΩ

(f) 1200°C
0.083A/cm²
Y1=Y2=0.2V/d
T=20msec/d
W(MP4)...R(MP2)
A(MP1)...R(MP2)
Cell discharged into 0Ω
Figure 7
Pt Electrode—Sodium Diborate

(a) 1200°C
0.083A/cm²; 50μF
Y¹=Y²=0.2V/d
T=5msec/d
W(MP4)...R(MP2)
W(MP4)...E

(b) 1200°C
0.083A/cm²; 50μF
Y=0.2V/d
X=1V/d
W(MP4)...R(MP2)
W(MP4)...E
V/q oscillogram

(c) 1200°C
0.200A/cm²; 50μF
Y¹=Y²=0.5V/d
T=5msec/d
W(MP4)...R(MP2)
W(MP4)...E
A(MP1)...R(MP2)

(d) 1200°C
0.083A/cm²; 50μF
Y¹=Y²=0.5V/d
T=2msec/d
W(MP4)...R(MP2)
W(MP4)...E
Recorded after current density measurements
Figure 7 (cont)

Pt Electrode-Sodium Diborate

(e) 1200°C
0.083A/cm²; 50μF
Y1=Y2=0.5V/d
T=2msec/d
W(MP4)...R(MP2)
W(MP4)...E
Immediately after 5min
dc at 0.083A/cm²

(f) 1200°C
0.083A/cm²; 50μF
Y=0.5V/d
T=2msec/d
A(MP1)...R(MP2)
Immediately after 5min
dc at 0.083A/cm²

(g) Reaction at Cathode on Left after Electrolysis in Sodium Diborate Melt
Figure 8
Pt Electrode-Sodium Diphosphate

(a) 1200°C
0.083A/cm²; 50μF
Y1=Y2=Y3=0.2V/d
T=5msec/d
W(MP4)...R(MP2)
W(MP4)...E
A(MP1)...R(MP2)

(b) 600°C
0.05A/cm²; 50μF
Y1=Y2=Y3=0.5V/d
T=5msec/d
W(MP4)...R(MP2)
W(MP4)...E
A(MP1)...R(MP2)

(c) 1200°C
0.083A/cm²; 50μF
Y1=Y2=0.2V/d
T=5msec/d
W(MP4)...R(MP2)
W(MP4)...E
10 min after 30 sec dc
at 0.083A/cm²

(d) 1200°C
0.083A/cm²; 50μF
Y=0.2V/d
T=5msec/d
A(MP1)...R(MP2)
10 min after 30 sec dc
at 0.083A/cm²
Figure 8 (cont)
Pt Electrode—Sodium Diphosphate

(e) 1200°C
0.083A/cm²
Y1=Y2=0.2V/d
T=20msec/d
W(MP4)...R(MP2)
A(MP4)...R(MP2)
Cell discharged into 10MQ

(f) 1200°C
0.083A/cm²
Y1=Y2=0.2V/d
T=20msec/d
W(MP4)...R(MP2)
A(MP4)...R(MP2)
Cell discharged into 0Q

Figure 9
Pt Electrode—Sulphuric Acid

(a) N-H₂SO₄
0.01A/cm²; 6µF
Oscilloscopic;
Platinum Wire

(b) 0.1N-H₂SO₄
17µA/cm²; 5µF
Direct Potentiometric;
Platinised Platinum
Figure 10

Ni Electrode-Alkaline and Buffer Solutions

(a) N-NaOH
0.01A/cm²; 10.6µF

(b) 0.2Μ-KH₂PO₄ + 0.2Μ-Na₃HPO₄ (pH6.8)
0.01A/cm²; 10.6µF

(c) 0.2Μ-KH₂PO₄ + 0.2Μ-Na₃HPO₄ (pH6.8)
0.01A/cm²; 10.6µF
After cathodic polarisation at 0.01A/cm² for 3min

(d) 0.1N-Na₅B₄O₇ (pH9.2)
0.005A/cm²; 10.6µF
After cathodic polarisation at 0.01A/cm² for 3min