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ELECTROCHEMICAL ASPECTS OF THE ELECTROFORMING OF IRON

by

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SUMMARY

The patent literature describing the development of the foil electroforming technology has been reviewed. A review of the literature covering the development of iron plating electrolytes has also been completed.

A detailed study of the effects of solution parameters on the conductivity of iron chloride solution and the effect of addition of a number of 'conductivity salts' has been carried out. The operation of a pilot plant for the continuous production of iron foil has been investigated and the parameters of foil production characterised.

Preliminary cathodic polarization studies were made at low current densities on the iron chloride electrolyte showing the effects of temperature on the system.

A number of possible materials for use as insoluble anodes have been investigated using anodic polarization to determine their behaviour in the aggressive hot iron chloride electrolyte environment. The possibility of reducing depassivation of the cathode by the addition of a less aggressive anion was studied but no significant improvement achieved.

For a more detailed and controlled study of the hot iron chloride electrolyte, a closed, divided-cell incorporating a rotating-cylinder electrode was designed and constructed to operate near to the boiling point of the electrolyte. The cell enabled a more rigorous study of the electrolyte to be made as the solution parameters could be better controlled.

The concentration of the ferric ion in the solution could be reduced and held constant while other factors could be measured. This system has been used to demonstrate the electrochemical reduction of ferric ion in addition to demonstrating that chemical reduction of the electrolyte was feasible and to study the effect of ferric ion concentration on cathode current efficiency. Control of ferric ion concentration by use of the divided cell has also enabled study of some of the deposition characteristics, the effects of stirring on the deposit and an investigation into the use of surface-active agents in further optimising the electrolyte performance.

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CONTENTS

II LITERATURE REVIEW - IRON ELECTRODEPOSITION

IV IRON FOIL PRODUCTION ON A PILOT PLANT

Chapter Page

V EXPERIMENTAL

VI RESULTS

VII DISCUSSION

VIII CONCLUSIONS

FIGURES, TABLES AND PLATES

APPENDIX 1 REGENERATION OF SPENT FERROUS CHLORIDE ELECTROLYTE

APPENDIX 2 SCANNING ELECTRON MICROGRAPHS OF IRON FOIL ELECTRODEPOSITS

I. INTRODUCTION

The researches described in this thesis arose from an industrial requirement that an attempt should be made to establish a deeper understanding of some of the electrochemical characteristics of the iron electrodeposition process, with particular consideration to the electroforming of iron foil from a hot iron chloride electrolyte.

Operational pilot plant production of iron foil had been achieved at the British Steel Corporation Research Laboratories in Swansea, and developed to production scale by Ironfoil Ltd., a subsidiary company of the Lee Group of Companies in Sheffield. It was in conjunction with the latter enterprise that the requirement to optimise the process and to examine some of the remaining problems arose.

The basic principles behind the deposition of thin iron sheet have been established for many decades. More recently, sound engineering methods have been developed to enable the efficient continuous production of iron foil. The areas that required more detailed understanding and possible optimisation were principally the electrical conductivity of the electrolyte and the electrochemical polarization characteristics of the hot (100°C), acidic iron chloride electrolyte used in this application. In addition to these areas of study, an effort was made to improve the quality of the product. The iron foil, although satisfactory in most respects, was not always of the highest possible quality. The major shortcoming being the occasional occurence of 'pinholing', caused it was thought, by the inclusion of solid particles in the foil during the electroforming process, which later became dislodged leaving minute pores in the foil. Possible solutions to this problem were examined.

Electroformed iron foil is a product of great practical significance. Studies carried out by the Lee Group of Companies indicated that the thinner gauges of foil (50-75 μm) could be electroformed at a cost that would be competitive with direct rolling of conventionally produced iron strip. Above this range, direct rolling is advantageous; below this range electroforming is cheaper and offers easier handling for very thin foil. Electroforming of iron foil has other advantages: the electrolyte can be made up by the dissolution of scrap steel in hydrochloric acid. This means that an efficient method is available for the recycling of scrap, such as black-plate trimmings, to produce a marketable product. Another possibility reviewed at length by Silman (1), is that the electrolyte could be prepared directly from the ore, perhaps on the site of a small user such as a packaging concern. In addition to producing foil economically, the cost of transport from a steel mill would be saved.

The packaging industry is only one of many possible markets for electroformed iron foil. Its high resistance to tension, tearing and impact, its impermeability to water, vapour and gas, its high melting point (1500°C), good electrical and magnetic properties, and the variety of finishes with which it can be produced, render it suitable and economic for many applications which already rely upon the use of other metallic foils.

The strength and impermeability of iron foil would allow its use for removeable foil closures such as milk bottle tops, yoghurt caps and oil can seals. Paper, board and plastic laminates of iron foil could be used in the construction of boxes, sachets, drums and tubes. A flat or corrugated ply of iron foil would have applications in heavy duty packaging. In the construction industry, iron foil could serve as a moisture barrier in various applications such as a facing for insulation, a substrate for bitumen damp course membranes, a lining under tiles or shingles and a decking amongst built-up roofing felt. The foil can be wound into flexible dustwork or formed into convolute tubing offering a high wall strength and dimensional stability to both heat and moisture.

The elctrical resistivity of iron foil is well suited for fabricating electrical resistance heating elements. The element's pattern can be readily etched or stamped on the foil. Copper coated iron-foil can be used for fabricating printed circuits. The thin copper coating acts as a conductive layer on the carrier of iron foil and results in an economic alternative to materials currently employed. The copper coated foil could also be used for fabricating the primary and secondary surfaces of heat exchangers. Iron foil could also serve as an electromagnetic shield for electrical components and cables, for example in T.V. tube electromagnetic shields and shadow masks.

Iron foil in its many possible finishes will attract magnets and as such would have many applications as magnetic wall boards, visual aids and games. In addition to the finishes already mentioned, it is also possible to coat the foil with zinc, polymer, lacquer and P.V.C. coatings.

Iron foil production comes from an union of the knowledge that has arisen from the development of the iron electrodeposition process and the foil production technology arising from the manufacture of thin copper and nickel foils. A review of the history of iron electrodeposition forms a main section of this thesis and is followed by an account of the development of foil production technology based on patent literature.

An opportunity was taken to operate the pilot plant, then available at the British Steel Corporation Laboratories in Swansea, to gain experience of real production on a small scale and to monitor the medium term behaviour of the electrolyte. It was originally intended to carry out a similar operation with the full-scale plant in Sheffield but this eventually proved to be impossible. Basic laboratory research was carried out to investigate certain important electrochemical parameters of the process solution, notably conductivity, polarization and solution redox stability, and these form the main part of the original work reported in this thesis.

II. LITERATURE REVIEW

IRON ELECTRODEPOSITION

(i) Introduction

Since Becquerel(2) first reported the preparation of iron by electrodeposition in 1831, the process has found numerous applications. The earliest applications included the manufacture of electrotypes and stereotypes(3) for use in the printing industry. This was of particular importance during periods of nickel and copper shortages as, for example, during World War II. An important and continuing application of iron electrodeposition has been in the building-up of worn or undersized components. The Russians in particular have developed this area(4).

The electrodeposition of iron has been developed to the state of commercial operation using a number of iron plating electrolytes. This field was initiated by the work of Burgess and Hambuechen(5) in 1904. They studied iron deposition from ferrous ammonium sulphate baths. Electrowinning of iron direct from ores was successfully developed during the second decade of this century. Eustis(6) working at the Massachuetts Institute of Technology conducted an investigation into the use of iron pyrrhotite ores in the manufacture of electrolytic iron up to pilot plant scale. This plant produced iron of better than 99.9% purity with sulphur as a by-product. This field was further developed at the Engels Copper Mining Company(7), resulting in the production of a practical cell for continuous operation in the production of electrolytic iron. Other notable commercial developments included the introduction of the 'Fischer-Langbein' electrolyte in Germany in 1908(8-14). This process has been extensively used, particularly during the First World War, to produce iron as a substitute for copper in military application.

One of the most promising applications of iron electrodeposition is electroformed iron foil. The attraction of the process lies in the possibility of direct manufacture of electrolytic iron from sources such as ore and scrap, and in the favourable economies of the procedure when compared with the alternative of rolling sheet to thicknesses of 0.1 mm and less. Many attempts have been made to produce iron sheet and foil on a commercial basis. Commercial production of iron sheet was reported in Vermont U.S.A. by Konrad in 1953(15). The plant produced iron sheet from pyrrhotite dissolved in hot iron chloride solution, giving a pure iron product with good ductility after low temperature annealing to remove hydrogen. The Montan-Union Company(16) used a continuous copper band as a base on which to deposit iron that could be separated in a later operation. Work at the British Steel Corporation Laboratories in Swansea, South Wales and later at the Electricity Council Research Centre in Capenhurst (see Patent Review Chapter III), has made significant advances towards successful commercial production of iron foil down to less than 25 µm thick. In both Company's operations, the electrolyte was obtained by dissolution of scrap iron in hydrochloric acid, and electrodeposited the iron onto a slowly rotating titanium cylinder from the hot (∿ 100°C) electrolyte. Good quality foil has been produced, but there remain some problems to be solved.

(ii) Reviews

As indicated above, iron deposition has a long and detailed history, and has been the subject of many hundreds of investigations. Many reviews and summaries of aspects of iron deposition have appeared in the literature, and as with other large areas of enquiry there have been many instances of duplication and overlap. The following reviews may be considered as being essential distillations of the work in the field of iron electrodeposition.

The initial and early work on both the laboratory and commercial production of electrolytic iron has been comprehensively reviewed by Cleaves and Thompson in their Monograph on Iron and its Alloys(17). Much of the work on iron electrodeposition has been of a very empirical nature, this is particularly true of the early work summarised in Cleaves and Thompson's Monograph. The basic working solutions were established during the period covered (1840-1935) and much experimentation was carried out in attempts to explore the many variables possible e.g. changes in the solution concentration, temperature, pH, addition of other salts.

A more detailed study of the electrolytes developed up to 1920 was made by Hughes(18). This review considered at length iron deposition from chloride, sulphate and mixed chloride/sulphate baths. A review with greater emphasis on the commercial aspects of electrolytic iron production was published by Belcher in 1924(19). In addition to summarising the progress made in the electrodeposition of iron over the previous seventy-five years, he considered the commercial manufacture of sheets and tubes.

Developments in the field upto 1940 were covered by Thomas(20), including descriptions of hot ferrous chloride and cold ferrous sulphate electrolytes and their applications particularly in printing. Some consideration was also given to the physical characteristics of the deposits produced from these electrolytes. In a similar vein, Lamb and Blum(21) have described the history of iron plating in printing. The review gave descriptions for ferrous ammonium sulphate baths and ferrous chloride/potassium chloride baths. The authors also reported investigations on the effect of iron salts and 'conductivity' salts on the nature of the deposit.

The most comprehensive of the more recent general reviews was compiled by Lamb and Thomas(22) in 1963 and revised and updated by Klingenmaier(23) in 1974. The usual general historical perspective was given followed by accounts of the development of the ferrous chloride and ferrous sulphate solutions. Some description of ferrous fluoborate and ferrous sulphamate baths were included in this review, and references made to the less common iron plating baths. These included alkaline iron plating baths, a mixed fluoborate sulphate bath and an iron (iii) oxide/sodium hydrochloride bath. In addition to this, the operation of commercial baths was discussed. Details of bath preparation, maintenance and control were given and references provided for further information on impurities, pH control, use of addition agents and methods of analysis for the electrolytes. The choice of suitable anodes, materials selection for tanks, and ancillary equipment, and finally the authors have compiled data on some of the properties of electrolytic iron. A much more detailed consideration of the properties of electrodeposited iron was made by Safranek(24) in 1969.

Walker and Irvine(25) have surveyed the production and use of electrodeposited iron including progress made up to the mid-seventies. The survey covered the development of iron electrodeposition and its major applications. An account of the more common baths was given, i.e. ferrous chloride, ferrous sulphate, ferrous sulphamate and ferrous fluoborate, together with a discussion of the effects of addition agents, impurities, pH and hydrogen uptake. Variation in the deposit properties with different solution parameters were given and a review of the production and use of iron alloys was made.

A recent short review from Russia(26) has surveyed the properties of iron electrodeposits and concluded that they were determined by the secondary processes of hydrogen evolution and the formation of insoluble basic compounds of iron as well as by the behaviour of the additives used and their degradation products.

A more specialised review covering the electroforming of iron components has been made by Lai and McGeough(27) at Aberdeen University. The major applications of iron deposition were covered from the early days of electrotype and stereotype manufacture; record stamper manufacture; electrorefining; foil and sheet manufacture; building-up of worn and undersized parts are all considered in good detail. The authors have also considered possible future applications of the process, for example, using it for high speed deposition as a backing material and nickel-iron alloy codeposition.

This review proposes to summarise the development of iron electrodeposition electrolytes and to indicate the characteristics of the electrolytes from which iron has been deposited. Emphasis is given to the more recent work since the older work has been well described and reviewed as indicated above.

(iii) Ferrous Chloride Electrolytes

The early development and establishment of the ferrous chloride from its origins in 1861, when Krämer$^{(28)}$ electrodeposited soft and ductile iron from a chloride electrolyte, to its established use by 1928, has been well described by Cleaves and Thompson in their thorough Monograph$^{(17)}$. These developments are summarised in Table 2.1, which is taken from that Monograph.

The Fischer-Langbein electolyte of that period (Patented in 1908, Refs. 8-14) is worth particular mention, as it has proven to be one of the more successful iron electrolytes. This combination of relatively high concentrations of ferrous chloride (400-700 g/ℓ) with the addition of calcium chloride and high operating temperatures (> 85°C) allowed relatively high current densities to be used (up to $\sim 3000\ A/m^2$) and low stressed deposits to be produced. The importance of the calcium chloride in the electrolyte would appear to have been overestimated in the literature as similar and better results have been achieved using a ferrous chloride only electrolyte.

Many modifications to the hot chloride electrolyte have been described since the establishment of the principle. Klingenmaier's review$^{(23)}$ has covered many of these, mainly involved with the replacement of calcium chloride by other alkali or alkaline earth salts, and their apparent effect on the nature of the deposit. For example, Stoddard(29) studied the effects of manganese chloride on the process and found that the grain size of the deposit could be controlled by appropriate addition. Max and Van Houten(30) carried out a much more detailed study of the properties of iron deposited from a ferrous chloride solution containing calcium chloride. They also did a systematic study on the effects of impurities such as copper, manganese and nickel on the physical properties of the deposit and found that the stress was reduced by small amounts of copper but that this adversely affected the ductility. Manganese and nickel were found to have a negligible effect in small amount. Similarly, the effects of small amounts of $AlCl_3$, $BeCl_2$ or $CrCl_2$ have been studied by Müller et al(31), who reported that these constituents were found to render the deposit softer and more ductile.

As stated, the chloride plating electrolytes were well established by the early decades of this century. No fundamentally new approach or major modification has arisen since. The majority of the work conducted in this area has been on minor modifications either to the constituents of the electrolyte or on changes to the electrolysis conditions with the intention of optimising the product parameters in line with the requirement of proposed applications. It would appear that most of the research in this area has been carried out by the Russians, in many cases with a view to the restoration of worn machine components. Melkov(32) has published work on the effect of calcium chloride on the current efficiency, microhardness and appearance of electrodeposited iron coatings, plated from a 200 g/ℓ. $FeCl_2 4H_2O$ electrolyte at 80°C at a current density of 4000 A/m^2. The results indicated that increased concentrations of $CaCl_2$ increased the microhardness of the deposit but had little effect on the current efficiency. At concentrations of greater than approximately 200 g/ℓ the coating became coarse and nodular and its adherence to the base deteriorated. Melkov returned to the problem of deposit adherence a few years later(33) in 1962 when he considered possible modifications of electrolysis conditions and substrate preparation techniques to improve deposit adhesion. He found that a deposit adhesion of more than 4500 kg/sq.cm could be achieved by pretreating the substrate with 30% H_2SO_4 and then plating with an initial current density of approximately 1000 A/m^2 for 3-5 minutes before increasing the current density to 4000 A/m^2.

Some of the work emanating from Russia was of a more technical than scientific nature, and concentrates on aspects of iron deposition such as methods of bath control, and was obviously intended as an aid to production rather than scientific development of the process. One such publication concerned the adjustment of the ferrous chloride electrolyte(34). This paper gave simplified methods for judging the pH of the bath by colour, and the relationship of the specific gravity of the electrolyte to the concentration of iron chloride and other alkali salts present. The ideas suggested would be of interest to the plant operator, but offer no suggestions for improvement of the process.

It would appear that little systematic work has been done in elucidating the basic characteristics and electrochemical properties of the solution from which to postulate and test ideas in a controlled manner. It is against this background that there has been a continuous stream of very empirical and limited scope work. Developments of this type continued through the sixties and as before have come mostly from Russia.

Petrov(35) and Pulatov(36) published work of a similar nature, having investigated the effects of the alkali salts potassium and sodium chloride, and manganese chloride on the cathodic polarization characteristics and grain size of the iron deposit. Petrov reported small increases (10-30 mV) in the cathodic polarization with addition of the above salts, and much greater increases in cathodic polarization of up to 100 mV with decrease in either electrolyte concentration and temperature. Pulatov's work essentially supported these findings, and went on to consider the effects of some variations in the electrolysis conditions on the quantity of hydrogen absorbed in the iron deposit. This work indicated a relationship between increased polarization and greater absorbed hydrogen. Thus, any factors which acted to increase the polarization , such as those mentioned above, tended to increase the amount of hydrogen found in the deposit.

In a later paper (1966) Petrov et al(37) looked at the effect of the rate of change of current density on the thickness of iron coatings and the productive capacity during programmed controlled electrolysis. The results cannot be said to be very significant as at rates of change of 300-800 A/m^2/min no change in the efficiency of productivity was observed while at lower rates of change a slight reduction in the efficiency was noted. This decrease was attributed to changes in the kinetics of the electrodeposition process, but since no solid kinetic or mechanistic considerations were presented this conclusion must remain in doubt.

Applications of the iron chloride electrolyte to jet plating have been made by Nitsa(38,39). In the first paper a method was described where a ferrous chloride/manganese chloride electrolyte was directed from a metallic nozzle serving as an anode onto a worn part which served as the cathode. Satisfactory plating was obtained at a current density of 3000-4000 A/m^2 and a pH of 0.5-0.7. The current efficiency achieved with this process was 80% which is lower than can be achieved with more conventional ferrous chloride plating. One possible reason for this relatively low current efficiency is the high level of ferric ion in the electrolyte. After short periods of operation its concentration was found to be approximately 15 g/ℓ, and is probably due to the inherently greater degree of oxidation that will occur with jet plating with this electrolyte. Attempts to reduce the degree of oxidation were made by addition of manganese chloride and a large improvement reported. The second of Nitsa's publications(39) dealt with the absorption of hydrogen by electrolytic iron deposits during anodic jet deposition from the ferrous chloride/manganese chloride electrolyte. The major conclusion of the work was that jet plating provided about a two fold reduction in hydrogen absorption into the deposit, when compared with deposition from a non-agitated solution. This result would confirm what one would intuitively expect, as the force of the jet impinging on the workpiece would reduce the formation and growth of hydrogen bubbles.

The mechanism of hydrogen bubble formation during plating from ferrous chloride was earlier studied by Karyakin et al(40). The formation and growth of the hydrogen bubbles on iron surfaces was filmed during deposition from a 500 g/ℓ ferrous chloride electrolyte at 20°C. Small changes in the pH of the electrolyte (0.1-4) and changes in the current density from 100-600A/m^2 did not appear to affect the process. The film also,showed that the bubbles formed preferentially at defects in the iron surface, and that the pores formed were sometimes filled up by later deposition, Those that were not were left as pits in the surface in the deposit.

The important area of hydroxide formation in iron chloride electrolytes was explored by Melkov and Namakonov(41) in 1969. Unfortunately, their work does not appear to be sufficiently technically advanced to tackle the problem satisfactorily. For example, the change in pH at the electrode interface was measured by removing the electrode from the solution and allowing the solution to the electrode to drain into a separate container where its pH was measured. This method allowed the solution to be affected by oxidation and change in temperature. Their conclusion that hydroxide formation in this electrolyte begins at pH's of approximately 2.1-2.2 at 75°C must be treated with some degree of suspicion as the pH is only one of the factors involved in the oxidation of ferrous solutions.

Fink et al(42) attempted to determine what were the principal variables in the electrodeposition of iron chloride electrolytes. Using polarization techniques they established that an increase in the overvoltage and current density caused changes in the type of crystal orientation from basis orientated to field orientated. They also found that at a constant potential the current density decreased with increasing pH upto a pH of 2.5 and then increased with increasing pH. The required overpotential for a given current density was found to decrease by increasing the temperature of the electrolyte in the region of 25-90°C. They also demonstrated that the current density at constant potential increased proportionally to the ferrous ion concentration. As with many previous researchers, Fink et al, examined the effects of addition of small amounts of foreign ions to the electrolyte. They indicated that additions of 10^{-3} to 10^{-1} g/ℓ of zinc or cobalt ions made no appreciable difference to the polarization characteristics in a 125 g/ℓ ferrous ion solution, but an addition of 10^{-1} g/ℓ of cadmium ions displaced the curve towards more negative potentials. Overall, they therefore confirmed that the pH, temperature and ferrous chloride concentration were the principal determinants of electrolyte characteristics.

The use of aluminium chloride as a pH buffer in ferrous chloride solutions has been suggested on occasions in the history of iron electrodeposition. The work of Freimanis and Apetenok (43) suggested that the addition of $AlCl_36H_2O$ improved the buffer properties of the iron chloride electrolyte and that the oxidation and 'aggressive' nature of the electrolyte are reduced. Other workers who have conducted surveys into the effects of aluminium chloride on the electrolyte and deposit are Müller et al (31) (already described) and Melkov and Namakonov (44) who also claimed that addition of this compound led to a more stable electrolyte.

Some more systematic studies of the electrochemical background, the kinetics and mechanism of the iron electrodeposition process have been conducted. These can be conveniently divided into two areas. Firstly, work on the fundamental kinetics and mechanism of the iron electrodeposition process. Much fundamental work has been carried out in this area and a later section of this Review is devoted to it. Secondly, many studies have been conducted which have contributed towards a greater understanding of the processes involved in the actual iron plating electrolytes, where parameters such as concentration, temperature and the degree of impurity are vastly different from the near 'ideal' solutions used in the former type of study.

As before, much work in this area has been done by Russians. In 1967 Nagirnyi, Bondar and Stender(45) published a study of the pH in the precathode layer as a function of the electrolyte layer, the structure of the deposit and the hydrogen overvoltage during the electrodeposition of iron from aqueous electrolytes without addition agents. A number of interesting findings arose from this work, mainly that the pH of the precathode layer corresponded to the regions of hydrate formation of ferrous ions at low ferric ion concentration, whereas at higher ferric ion concentration (i.e. after the solution has had prolonged contact with air) the pH in this layer was controlled by the region of ferric ion hydrate formation. The cathode depositsin acid solutions were found to have identical structures, but when deposited from solutions at pH 2.0, a laminar structure could be observed, apparently because of the inclusion of iron hydroxide in the deposit.

More recently (1976) Melkov and Shvetsov(46) studied some of the variables involved in convective streams in highly concentrated iron chloride solutions. A number of factors and related variables were established. These included the variations of solution density with temperature, the relationship between convective stream velocity and temperature and the relationship between the electrical resistance in the cell and the electrolyte concentration, kinematic viscosity and temperature. The authors concluded that the optimum conditions for plating iron in a purely convective situation were obtained using an iron chloride concentration of 310 g/ℓ at 75°C. Modern polarization methods were used by Namakovov and Melkov(47) to study the buffer capacity of iron chloride solutions containing large additions of aluminium chloride. They found that maximum buffer capacity at a pH of 0.5 was in a bath containing 100 g/ℓ $AlCl_3 6H_2O$ and 300 g/ℓ. $FeCl_2 .4H_2O$ at 75°C, and the minimum was in a bath containing 500 g/ℓ of $AlCl_3 6H_2O$. They also determined that the current efficiency of iron deposition decreased by 6-8% after the addition of the aluminium salt owing to an increase in hydrogen evolution. This is an important factor when considering the economic factors involved in the design of an iron electroplating system. Finally the authors concluded that for high quality electroplating where close control of pH with high buffer capacity was required, a solution with a concentration of < 300 g of $AlCl_3 6H_2O$ and 300 g/ℓ $FeCl_2 .4H_2O$ was optimal.

In summary, the ferrous chloride is now reasonably well established and characterised. Its major applications are in the areas where high rates of deposition are desired since the high solubility of this salt, the high temperatures at which it can be operated and the good conductivity of the electrolyte permit relatively high plating rates. The ferrous chloride electrolyte does, however, have some drawbacks. The extent and significance of these will depend on the application. One of the major disadvantages of the electrolyte is its corrosive nature. This means that choice of materials for plant construction is critical, ventilation of the plant area is important and that some precaution is exercised by plant operators. Another point worthy of consideration in connection with this electrolyte is that there is always some degree of hydrogen evolution taking place in conjunction with the deposition process. Great care must be exercised to maintain good control of the electrolyte so that hydrogen evolution and and thus hydrogen embrittlement of the deposit is minimised.

(iv) Ferrous Sulphate Electrolyte

Electrolytic iron has been produced from sulphate baths by a number of investigators. A satisfactory process for 'steeling' electro-types was reported by Klein(59) as early as 1867. As with the chloride based electrolytes, the early progress in sulphate based electrolyte development has been well reported by Cleaves and Thompson(17). The essential details of a number of the early sulphate solutions are summarised in Table 2.2, which is taken from the Cleaves and Thompson Monograph.

The early workers established the characteristics of this electrolyte, the most significant being that the limited solubility of this salt so restricted the permissible current density that the rate of deposition of iron was very slow. It was found that additionsof magnesium sulphate, sodium bicarbonate, sodium sulphate, ammonium oxalate and ammonium sulphate improved the electrical efficiency of the electrolyte but tended to contaminate the deposit. Better success appears to have been obtained from solutions of ferrous ammonium sulphate than from the other sulphate baths; a solution of this salt was used by Burgess and Hambuechen(5), who were the first to produce electrolytic iron in quantity.

More recent work is adequately covered in Klingenmaier's review(23), which compares some of the different sulphate electrolytes and provides key references to some of the more important work carried out up to that time (1974).

The ferrous sulphate electrolyte has continued to attract interest and attention particularly because of its non-corrosive nature and ability to produce a reasonable deposit at or near to room temperature. Although the optimum current density possible with this electrolyte will always be lower than the hot chloride electrolyte, investigations have continued to examine ways of improving this parameter. Kudryavtsev and Yakovleva(69) were able to produce a relatively non-corrosive electrolyte consisting of 280-420 g/ℓ of $FeSO_4.7H_2O$ and 100g/ℓ of $Al_2(SO_4)_3.18\ H_2O$ with a pH of 2.5-3.0. At a temperature of 20-40°C hard iron deposits were obtained at an optimum current density of 300-800 A/m^2 in an unagitated solution and 500-1200 A/m^2 with stirring. This solution could also be operated at 1500-1800 A/m^2 if the temperature was increased to 70°C.

Further researches in the Soviet Union(70) suggest that the cold ferrous sulphate electrolyte may be advantageous for electroplating components of complex shape. The plating rate is slow, taking up to 100 hours of continuous deposition to obtain a 0.5 mm.thick deposit, but the solution is stated to have good throwing power, and gives a reasonable deposit with a low hydrogen content. The main constituent of the electrolyte suggested for this purpose was 180 g/ℓ of ferrous sulphate. In addition to this, the researchers have examined the effects of other constituents in minor quantities. They found that the addition of 10g/ℓ of $NaBF_4$ and $(NH_4)_2SO_4$ made possible the production of soft, ductile deposits, the mechanical properties of which were almost independent of the current density. Addition of 0.5g/ℓ of sulphonated phenol was found to increase both the hardness and the ductility of the metal deposits, but both properties decreased with increased concentration of the additive.

The successful work of Burgess and Hambuechen in the development of the ferrous ammonium sulphate electrolyte has already been mentioned(5). Later workers have further developed this area. Kapoor et al at the Indian Institute of Technology (71)have successfully operated a bath composed of 350g/ℓ ferrous ammonium sulphate, together with small amounts of ammonium citrate and aluminium sulphate. The combination of ferrous ammonium sulphate and aluminium sulphate gives a bath that is fairly stable against atmospheric oxidation. Operated at 70°C and a pH of 3.0-3.5, the optimum current density was 500 A/m^2 with a cathode current efficiency of 90-95%.

Nagirnyi, Bondar and Stender(72) have investigated the properties and structures of deposits, current efficiency, pH of the cathode layer and cathodic polarization during deposition of iron at room temperature from ferrous sulphate solutions with and without additions of ammonium sulphate. They were able to obtain good quality deposits with a current efficiency of 96-98% at current densities of up to 1000 A/m^2 with the presence of ammonium ions. The authors determined that with ammonium ions present, the pH of the cathode layer reaches approximately 9, indicating that iron ammines may be formed near to the cathode. Their polarization studies gave potential versus log current curves that were linear with a slope of 60 mV/dec. in pure solution and 110-130 mV/dec. in solutions with NH_4^+ additions. A significant role of crystallisation phenomena, besides the discharge of ions, is indicated.

The extent of hydrogen absorption in iron deposits from sulphate solutions has been studied in some detail by Bubelis et al(73,74). The amount of hydrogen codeposited with iron was determined by vacuum extraction at ∿ 300°C. The maximum absorption occurred at lower temperatures with decreased amounts absorbed as the electrolyte temperature was increased. Additions of small amounts of sulphate compounds such as

Na_2SO_4, $MgSO_4$ and $Al_2(SO_4)_3$ were found to decrease hydrogen absorption. The effects of periodic interruption and periodic reversal of the current were also examined. Periodic interruption was shown to decrease the degree of hydrogen codeposition, but reversing the current only decreased the hydrogen absorption when an oxidising agent such as $K_2S_2O_8$ was added to the electrolyte.

Some of the factors affecting the inclusion of foreign particles in iron deposits from sulphate solutions have been examined by Vengris and Bubelis(75) and later by Vengris et al(76). The basic conclusions of the published work appears to be that the amount of particle inclusion in the deposit depends upon the rate of formation of basic compounds at the cathode, thus an additive which increases the concentration of these compounds will be detrimental in this respect. $Al_2(SO_4)_3$ and H_3BO_3 are included in this category. It is worth noting that the former compound is particularly mentioned in this context, as it has found much application.

The effect of aluminium and other ions (magnesium and ammonium) on the value of the electrolyte pH, particularly in the region of the catholyte layer has been studied by Orszag(77). The use of a glass microelectrode facilitated these studies in a 0.8 M ferrous sulphate electrolyte using 0 - 0.8g-ion/ℓ additions of the ions mentioned. The ammonium ion was found to give a lower value of pH in the catholyte due to the buffer action of $(NH_4)_2SO_4$, while Al^{3+} and Mg^{2+} ions led to an increase in catholyte pH. The presence of $Al_2(SO_4)_3$, the catholyte reached the limit pH of $\sim$4 probably due to the formation of iron hydroxides.

In addition to work of type described above, studies of a more fundamental electrochemical nature have been conducted on the ferrous sulphate electrolyte. Levin and Pushkareva(78) studied the current efficiency of iron deposition and hydrogen evolution, and the current density as functions of the potential in a 200g/ℓ $FeSO_4.7H_2O$ based electrolyte. They were able to relate the ratio of the current efficiency for iron deposition and hydrogen evolution versus the potential to three distinct types of deposits. The first was iron with a column like structure, the second, a dense iron deposit, and the third to the deposition of powder. Current versus potential studies were interpreted as indicating the formation of $Fe(OH)_2$ at a point below the theoretical pH of 6.7. The pH of $Fe(OH)_2$ formation was found to decrease with increasing electrolyte concentration, which was attributed to the formation of slightly soluble compounds of the type $FeSO_4.2Fe(OH)_2$. $(3FeO.SO_4.2H_2O)$. From their findings the authors have suggested that the effects of concentration and pH could be used to control the formation of iron hydroxides and thus the deposit properties.

Matulis and Bubelis(79) have conducted some polarization studies of the ferrous sulphate and ferrous ammonium sulphate electrolytes. Changes in the polarization potential were found to be a function of the ferrous sulphate concentration, the pH and the degree of solution agitation. In more acidic electrolytes the deposition process involved a discharge of hydrogen ions which increased the pH of the near cathode layer causing the formation of a colloidal film of ferrous hydroxide which resulted in an increase in the polarization potential as the active centres of deposition are partially blocked.

Further studies of the polarization characteristics of ferrous sulphate electrolyte have been made by Rotinyan and Sysoeva(80). The cathodic polarization and double layer capacity of 0.19 - 0.93 M ferrous sulphate electrolytes containing additions of sodium chloride and boric acid, were determined at a number of temperatures between 25°C and 70°C. The information obtained was used to calculate Tafel parameters giving a'b'value in the Tafel equation equal to $2.3RT/\alpha zF$ and varied between 0.06 and 0.08V, increasing with temperature; α values were 0.45 ± 0.05 and were independent of temperature. The energy of activation for the deposition of iron was also calculated as 17 kcal/mole.

The ferrous sulphate electrolyte therefore offers the possibility of operation at low temperature, with relatively low susceptibility to oxidation. Its limitations in terms of maximum operable rate of deposition preclude its use in applications necessitating high rates of deposition (such as foil electroforming). Its principal areas of application have included building-up of undersized machine parts(81,82) and to apply a hard facing to stereo types(21).

(v) Mixed Sulphate-Chloride Electrolytes

The development of this electrolyte evolved from efforts to combine the rapid deposition capabilities of the ferrous chloride electrolyte with the less aggressive nature of the ferrous sulphate electrolyte. The first proposals for this type of bath appear to be due to Meidinger(83) in 1859 and Varrentrapp(84) in 1868, who described electrolytes composed of ferrous sulphate and ammonium chloride for use in 'steeling' electrolytes.

The initial work on the sulphate-chloride electrolyte is reviewed in Cleaves and Thompson's Monograph(17), the more significant publications of that period are summarised in Table 2.3. It is interesting to note that a review by Hughes(18) in 1921, comparing the mixed sulphate-chloride bath with the single chloride or sulphate baths concluded that the mixed bath had no points of superiority over the single anion electrolyte and had certain disadvantages such as difficulty of control, not present in the simpler baths.

Later work by Schaffert and Gonser(87), reported considerable success in the development and operation of a sulphate chloride bath even to the extent of successful commercial operation. Their investigations into the behaviour and properties of this type of bath led to the solution of an electrolyte consisting of 250g/ℓ of ferrous sulphate, 42g/ℓ of ferrous chloride and 20g/ℓ of ammonium chloride as being most suitable to electrotyping and for surfacing stereotypes. An adequately ductile, smooth deposit could be produced at temperatures below 50°C. The ability to produce a satisfactory deposit at relatively low temperature is important in this application since a considerable amount of work is done with wax or plastic mould cathodes.

An interesting application for the mixed sulphate-chloride bath has been suggested by Beach(88), this is the use of the bath to provide a starting deposit on active metals such as aluminium, beryllium or uranium. The bath can also be used for applying an intermediate layer of iron between steel and electrodeposited antimony. It has been stated that the use of iron in this application promotes uniform coverage and adhesion of the antimony deposit(89). In addition to the basic iron sulphate and chloride mixture the bath described contains small amounts of boric acid and sodium formate.

A number of investigators have studied the physio-chemical properties of iron deposits from sulphate-chloride electrolytes. Petrov and Andreeva(90) determined the effect of 50-200g/ℓ additions of $FeCl_2.4H_2O$ to 200-400g/ℓ solutions of $FeSO_4.7H_2O$ on the current efficiency and the microhardness of the deposits. At current densities of 1500-2500 A/m^2 and temperatures of between 30-70°C, the microhardness was found to increase by a factor of 1.5-2.0 with addition of 50-100g/ℓ of ferrous chloride to the sulphate electrolyte. The current efficiency of the process was similar to levels attained with a chloride only electrolyte. The rate of deposition was found to double for additions of ferrous chloride up to 100g/ℓ $FeCl_2.4H_2O$ and then levelled off.

Levy and Levy et al have conducted a number of studies on the effects of various solution parameters on the physical properties of iron deposited from this mixed electrolyte. Levy(91) has published a study on the effect on the internal stress of the current density, temperature, pH and chloride ion concentration. The internal stress was shown to decrease with increasing temperature and pH. It increased with increasing current density and was found to be virtually independent of chloride ion concentration from 15-30g/ℓ. The paper also draws attention to the fact that while the various deposition parameters, when considered singly, can be explained satisfactorily, there can be a complex intermingling of these parameters. Acting simultaneously, they determine the state of the cathode layer and processes occurring at the cathode solution interface and consequently, the structure, internal stress and properties. Levy et al(92) also studied the effects of the above parameters on the microstructure and microhardness of the deposit. They found although there was a significant change in the microstructure with increasing solution pH, the microstructure was not greatly affected by changes in the other deposition parameters. Their further researches into the microhardness of the deposit confirmed the findings outlined in Levy's previous paper(91) considered above.

Other electrolyte and deposit characteristics have been examined by Koshmanov et al(93), these included the cathodic polarization and crystal size of iron as functions of the concentration of various inorganic additives e.g. $Al_2(SO_4)_3$, Mn, Ni and Cd ions and H_3BO_3. Andreeva(94) has researched into the formation of hydrates in the mixed sulphate-chloride electrolyte in addition to the chloride and sulphate only electrolytes. Optimum electrolyte composition and electrolysis conditions to minimise hydrate formation were discussed.

(vi) Ferrous Fluoroborate Electrolyte

The ferrous fluoroborate electrolyte is a more recent development than the previous electrolytes described. It arose during World War II when scarcity of nickel promoted the development of fluoroborate solutions for the electroforming of iron, principally for the electroforming of stereotypes for the printing industry(95). Early descriptions and patents of fluoroborate electrolytes include Kudryavtsev and Mel'nikova(96) who described a solution based on 300 g/ℓ ferrous fluoroborate with additions of boric and fluoroboric acids to buffer and control the electrolyte. A good quality deposit could be obtained from this oxidation resistant electrolyte at current densities of between 200-1200 A/m^2 providing that the solution parameters such as pH were well controlled. Poor(97) patented fluoroborate electrolytes based on mixtures of ferrous fluoroborate and ferrous chloride and ferrous fluoroborate, ferrous sulphate and ammonium chloride. In a similar vein, the bath mentioned above(95) and described in a Baker and Adamson Product Bulletin(98), was based on a mixture of ferrous fluoroborate and sodium chloride.

All of these electrolytes were capable of producing deposits with adequate strength, hardness and ductility and offered the additional advantages of being more stable and resistant to oxidation, having the capacity for operation at lower temperatures with less aggressive tendencies than the chloride electrolytes and the ability to produce satisfactory deposits at higher current densities than the sulphate based electrolytes.

The work on the ferrous fluoroborate electrolytes described so far served to establish the basic electrolyte in a number of variations. Much of the work done since has been conducted in an effort to determine the effects of the fluoroborate electrolyte parameters on the deposit and to try to determine which solution gives the optimum performance in a required application.

Schultze(99) worked on the optimisation of a fluoroborate bath containing no sulphates or chlorides, using conditions and organic addition agents derived from experience of nickel electroplating. It was found that a good iron deposit could be obtained at a temperature of 60°C and a current density of approximately 1000 A/m^2, and the physical properties of the deposit could be enhanced by the addition of the organic addition agents used in nickel electrodeposition.

Gindlin and Moseev(100) conducted a study specifically into the dependence of current efficiency and microhardness of iron deposits from fluoroborate electrolytes on the cathodic current density, pH, temperature and concentration of HBF_4 and H_3BO_3. The current efficiency varied between 76 - 97% depending on conditions and increased with increasing current density, temperature and salt concentration and with decreased acidity. The microhardness of the deposits varied between 300-575 kg/sq.mm, increasing with increased current density and acidity and decreasing with increased concentration and temperature.

Further studies of this nature have been conducted and comparisons made between the characteristics of iron deposition from fluoroborate electrolytes and the deposition of other iron group metals from this electrolyte(101-104). The first paper(101) also compares the properties and operation characteristics of lead, tin, tin-lead alloy, cadmium, indium and zinc fluoroborate electroplating baths.

Levy et al have published two papers(105,106) surveying the electrodepositon and properties of iron deposited from mixed chloride/fluoroborate baths. In these they have considered the effects of the electrolyte parameters and operating conditions on the quality of the iron deposit. In the first paper(105), an attempt was made to correlate the mechanical properties and microstructures of iron foils with a variety of combinations of current density, temperature and pH. They succeeded in producing foils having an ultimate average tensile strength of 120,000 p.s.i. The second publication(106) covers much of the same ground, but has gone on to use optical and electron microscopy to confirm the results of the experiments on mechanical properties. These methods of study led to the observation of a relationship between the surface roughness of the deposit and the bulk pH of the electrolyte, which was explained in terms of hydrogen evolution and hydroxide precipitation.

The theme of the influence of the formation of insoluble hydroxides on the structure of the iron deposit from the fluoroborate bath was taken up again by Radziuniene and

Bubelis(107). They proposed that the formation of these insoluble compounds effected the structure by blocking active growth centres and that a decrease in the concentration of these compounds led to a more brittle and disorientated deposit.

Studies of the deposit stress(108) and of a fluoroborate plating process capable of producing low stress deposits(109) have been carried out. The former paper discussed the use of X-ray techniques as a tool for the study of internal stresses during electrodeposition and other methods for the continuous measurement of stresses. Their work on iron showed that the stress decreased as the thickness of the deposited layer increased. This result confirmed the usual findings concerning stress in metal electrodeposits where the stress is usually greatest at the deposit/substrate interface. The latter paper(109) concentrated on the development of a fluoroborate bath that would produce a good quality low stress deposit without the use of organic addition agents, since their degradation products often give rise to problems. A purified fluoroborate bath consisting of 55.4 g/ℓ Fe^{3+} and 9.1 g/ℓ NaCl, operated at a pH of 3.0-3.7 and a temperature of 57-63°C was found to satisfactorily fulfil the requirements, provided that the bath was carefully maintained by constant filtration.

Further research on the optimisation of the fluoroborate bath for use in applications where its less aggressive properties are required, is reported by Mueller et al(110). These workers described the satisfactory operation of a fluoroborate only bath at a pH of 2.0-2.5 and temperatures of 60°C again with continuous filtration to keep the electrolyte contamination to a minimum.

A short summary of fluoroborate electrolytes including a brief description of the use and application of the ferrous fluoroborate bath has been made by Benninghoff(111), although no further references are provided.

(vii) Ferrous Sulphamate Electrolyte

As with the fluoroborate electrolyte, the ferrous sulphamate electrolyte is a relative newcomer to the field of iron electrodeposition. It appears to have been first reported by Piontelli(112) in 1943, who claimed that deposits with very good properties could be obtained from 0.5-1.0 M solutions of iron(II) sulphamate at 25°C and at a current density of 300 A/m^2. A similarly favourable report was made by Barrett in 1960(113), on the results of iron deposition from a bath comprising of 400 g/ℓ iron sulphamate and 30 g/ℓ of ammonium sulphamate with small additions of hydroquinone or formic acid. Current densities of up to 1000 A/m^2 and cathode efficiencies up to 96% were described by Misra and Rama Char(114) in another bath containing both iron and ammonium sulphamate.

Studies by Mazza et al at the Milan Polytechnic(115,116) have indicated that iron can be deposited from this electrolyte at current densities of 2000-2500 A/m^2. This showed that the sulphamate could have applications in high speed electrodeposition as an alternative to the ferrous chloride electrolyte, although factors such as cost must also be considered.

At such high current densities the authors found that it was necessary to provide strong agitation and to use wetting agents to avoid pitting. One drawback noted was that the throwing power of the sulphamate electrolyte was very low, often giving rise to very uneven metal distribution on the cathode.

The most systematic survey of the characteristics of the iron sulphamate bath has been published as a series of papers (117-121) from the Government Industrial Research Institute, in Nagoya, Japan. The first of these(117) studied the effects of the concentration of the additives urea and boric acid and the effects of solution parameters such as ferrous ion concentration, pH, temperature and current density on the current efficiency and surface characteristics of the deposit. Both of the additives were found to act both as brighteners and as buffers. Their use enabled the production of bright, crack and pit free deposits. Another bath additive considered by these researchers was ammonium bifluoride(118). They claimed that its use prevented the generation of cracks and pits in the deposit, but had no beneficial effect on brightness. In addition to the above work, the Institute has carried out a significant survey of the factors determining the internal stress of iron deposits from sulphamate electrolytes. The effects of organic addition agents in the ammonium bifluoride containing electrolyte were studied(119) and suggestions for optimum levels of addition made. The effects of foreign ions on the internal stress were also examined(120). The addition of Na^+, K^+, Ca^{2+} and Al^{3+} did not effect the internal stress, whereas Co^{2+}, and Ni^{2+} were found to increase the internal stress as their concentration increased. Results published in the same paper also indicated that the complex ions TiF_6^{2-}, SiF_6^{2-}, BF_4^-, ZrF_6^{2-}, BeF_4^{2-}, WO_4^{2-} and $Mo_7O_{24}^{6-}$ also increased in stress. In a follow-up to this work, the effects of some common anions on the internal stress were investigated(121). An increase in the amount of NO_3^- and PO_2^{3-} increased the deposit stress, whereas the addition of PO_4^{3-} on $P_2O_7^{4-}$ reduced the stress. The results of other studies reported in the same paper indicated that internal stress reached a maximum at lower values of pH and temperature, so that for optimum deposit characteristics, the pH should be above 2.0 and the temperature approximately 50°C.

Finally, a general survey on the properties of iron deposits obtained from sulphamate electrolytes was published by Sadakov and Burygina(122) in 1976. They showed that depending on the concentration of addition agents, the iron salt, the pH temperature and current density, iron deposits could be obtained at a current efficiency of 78-95% with a internal stress of 1-25 kg/mm^2, hardness 220-600 kg/mm^2 and sulphur content of between 0.01-0.07 wt%.

(viii) Less Common and Special Purpose Electrolytes

A number of iron plating electrolytes based on unusual salts, organic compounds and molten salts have been described in the scientific and technical literature. Most are unlikely to be of great interest to the practising electroplater, but merit inclusion in this review as some may well indicate the direction of future developments in this field.

The copper pyrophosphate electrolyte is already well established in the field of copper electrodeposition, and reports have been made to use that anion as the basis of an iron deposition electrolyte. Case and Krohn(123) electrodeposited iron-molybdenum alloys from pyrophosphate solutions, but the first reports of iron deposition from this electrolyte come from Sree and Rama Char at the Indian Institute of Science, Bangalore(124). The authors showed that the pyrophosphate bath could be used to deposit iron over a range of experimental conditions. Some problems were experienced with anode passivity, and as with other complex salt baths the cathode polarisation was high. It is worth noting that the main constituent of this bath when operated at optimum conditions is iron (III) pyrophosphate, therefore a further penalty in terms of power requirements occurs during the deposition process.

Other baths based on complexes of iron (III), such as oxalate and citrate have been described(125); this type of bath, however, is useful primarily for electroanalysis rather than electroplating. Another reference to an alkaline iron plating bath (in addition to the pyrophosphate bath) is one in which iron (III) is complexed with triethanolamine and ethylenediaminetetraacetic acid(126). Only thin deposits have been reported from this bath and like the pyrophosphate bath iron does not dissolve in it anodically. The deposition of iron powder from a slurry of Fe_2O_3 in caustic soda has been investigated(127) and operated at pilot plant level. A similar bath has been described Wranglen(128) which consisted of an aqueous solution of iron (III) oxide and sodium hydroxide, in which the iron was probably present as sodium ferrate.

Much interest has been shown in the Soviet Union in iron deposition from organic electrolytes. Electrolytes based on methyl sulphate have received the most attention and a number of papers have been published describing variations of this electrolyte, its properties and the characteristics of the deposits produced(129-137). One of these papers(136) included a comparison of the properties of the methyl sulphate containing electrolyte and sulphate and chloride containing electrolytes and concluded that some of the physiochemical properties of the iron deposits such as microhardness, adherence to the substrate and brightness were improved by the use of the organic based bath. However, it should be made clear that this type of bath would not merit serious consideration for practical high speed deposition on grounds of cost and electrical conductivity.

Other organic based iron electrolytes have been reported. A method for the preparation and use of iron (II) phenolsulphonate to deposit iron was reported as early as 1958(138). This electrolyte has been used to deposit very hard iron coatings(139,140) at current densities of up to 1500 A/m^2. It has been electrodeposited as a powder from a solution of ferrous sulphate dissolved in the organic reagent dimethyl sulphoxide(141). However, it is arguable whether work of this nature can be defined as 'organic' due to the highly polar nature of this reagent.

It has proven possible to obtain iron electrodeposits from iron perchlorate electrolytes(142), and from iron salts of fluoro acids such as H_2PO_3F, HPO_2F_2, HPF_6, CF_3COOH and C_3F_7COOH(143). The deposits produced were usually not sound and were generally much inferior to those from standard sulphate or chloride baths.

A systematic discussion of the deposition of iron from molten salts and iron oxide melts is outside the scope of this review, but iron has been successfully electrodeposited from a number of melts, and some useful electrochemical data are available(144-148).

(ix) Organic Addition Agents

Many of the papers already reviewed in this chapter have included information on the use and effects of certain organic addition agents. There is a large literature concerned with this field, stretching back to the origins of iron electrodeposition. The early developments are discussed in Cleaves and Thompson's Monograph(17), and further information may be obtained from the subsequent reviews referred to earlier in this chapter.

The papers published in this area that have not been considered in previous reviews can be divided into two main areas. Firstly, those concerned with a general treatment of organic addition agents and secondly, those concerned with specific additions agents. The latter group forms by far the majority of the publications.

The general papers include a study of the effects of additives and electrolysis conditions on the hydrogen content of iron coatings and current efficiencies for iron and hydrogen(149). Popereka and Kosamanov(150) have examined the influence of additives on the internal stresses of the deposit and on the degree of inclusion into the deposit of degredation products of carbon and sulphur containing addition agents. Further studies of this nature were carried out by Matuliauskiene et al(151) who looked into the behaviour of additives at the cathode during the electrodeposition process. The actual effect of organic additives on the kinetics of the cathode process was examined by Petrov(152). This work considered the effect of the additives on the potential of an iron cathode in a concentrated iron chloride based electrolyte. The potential increased with the concentration of additive, passed through a maximum value and decreased slightly to a constant value. Specific values of the change in potential are given for various additives, and the effect of these compounds on the evolution and inclusion of hydrogen was studied.

The remaining papers, as previously mentioned, are primarily concerned with the study of individual addition agents or related groups of compounds on the iron electrodeposition process. Urea and thiourea have been the subject of many studies. Their effects on iron deposition from an iron sulphate bath has been discussed by Machu and ElGhandour(153). The kinetics of these organosulphur additives' interaction with the iron electrode has been examined by Vegys et al(154). Proposed equations which described the deposition of additives and metals were tested experimentally, and effects on the surface activity of the electrode determined. Further studies into the behaviour of thiourea in electrolytes have been made(155-157) with emphasis on the effects of incorporation of degradation products into the deposit. The last of these studies(157) used polarographic methods to yield kinetic parameters for the iron deposition reaction.

Other sulphur-containing addition agents made the subjects of research include the behaviour of p-toluenesulphoric acid in iron sulphate electrolytes(158), and the behaviour of sulphanilic acid(159) and sulphite and thiosulphite ions(160).

The effect of nitrogen containing addition agents has been studied by Soviet research groups. Kudryavtsev and Smirnova(161) insvestigated the electrodeposition of iron from electrolytes containing aminoacetic acid, which was found to markedly decrease the crystal size in the deposit, and to improve the electrolyte stability by raising the threshold of $Fe(OH)_3$ formation by air oxidation. The effects of a number of nitrogen containing additives (and other organo-compounds) on the electrocrystallization of iron from sulphate based electrolytes was examined by Radzuiniene et al(162), using electron microscopy. The authors suggested that the structure of the iron deposit depended not only on the adsorption of the additives and their reaction products, but also on the changes in the amount of basic iron compounds and the way that they were dispersed on the anode surface. A similar suggestion has been proposed by Vengris et al(163), as an explanation into the inclusion of impurities into iron deposits from electrolytes containing organo-nitrogen compounds.

Other organic compounds that have been investigated as potential agents include ascorbic acid(164), acetylinic compounds, derivatives of aromatic unsaturated acids and polycarboxylic acids(165), glycine(166) and urotropine and tribenzylamine(167).

Finally, a number of projects have looked into the effects of organic addition agents on the hardness or wear resistance of iron deposits(168-171). These were all carried out to determine the effect of various common bath additives e.g. dextrin, gelatin, citric acid and glycerol, on the wear resistance of iron parts in practical ferrous chloride electrolytes used for the restoration of worn machine components.

It is clear that a large number of additives have been used, often in a superficial and empirical manner and little attempt has been made to consider such additives in a systematic manner or in relation to theories for the electrodeposition of iron. It is therefore reasonable to conclude that addition agents for iron plating have not been considered in depth and indeed that the work done is small in comparison with studies of addition agents for mickel electrodeposition, where the majority of addition agent work has been done.

(x) Electrical Conductivity

Accurate information on the conductivity of concentrated

ELECTRICAL CONDUCTIVITY

Accurate information on the conductivity of concentrated solutions of iron salts is difficult to obtain. A general survey of the conductivity and density of aqueous solutions of about sixty metallic salts (including iron salts) of inorganic and organic acids was compiled by Heydweiler in 1921 (172). The only information available in that publication is a measurement of the conductivity of three concentrations of ferrous chloride at 18°C, which is clearly insufficient to provide enough information for modern requirements.

The remaining and more recent investigations of iron electrolyte conductivity have come from the Soviet Union, but have been limited in both their availability, because of a lack of translations, and in their scope in that no attempt has been made to relate the importance of the electrical conductivity with other important solution parameters and polarization characteristics.

The first of these papers was published by Piyavskii (173) and dealt only with the electrical conductivity of cold iron plating electrolytes and concludes that for industrial purposes the chloride salt at a concentration of 400 g/ℓ without any conducting additives gives the optimum electrolyte.

An interesting and reasonably detailed survey of the electrical conductivity and viscosity of concentrated iron chloride solutions (up to 700 g/ℓ) was carried out by Shvetsov and Melkova (174). This survey has provided much useful data; however, it was carried out in the temperature range of 40-80°C, and therefore does not provide the necessary data for near boiling electrolytes.

Similar information has been provided by Kosov and Nikolaev(175), who have concentrated at the lower end of the temperature scale (20-60°C), but have compiled conductivity on data for the sulphate and sulphate-chloride electrolytes in addition to the chloride-only electrolyte.

(xi) Use of a Divided Cell in Iron Electrodeposition

The use of a porous diaphragm in this context was reported as early as 1895 by Hoepner and Klie(60), who utilised the device to aid the deposition of iron from a ferrous sulphate solution. Since then it appears to have been essentially ignored until quite recently when the use of a porous diaphragm was reported by Kudryavtsev et al(176) in an experimental iron plating bath where a diaphragm was used to separate copper cathodes from platinum anodes. Its application appears to have been quite successful, and it is worth noting that this paper draws attention to the fact that if the insoluble platinum anodes were replaced by soluble anodes, then a diaphragm was no longer required. (This point is discussed later in this thesis).

Patents have been issued to two groups of Japanese workers (177,178) concerning the application of ion exchange membranes to iron solutions. The first was connected with the use of a cation exchange membrane in a ferrous sulphate electrolyte using an insoluble anode and sulphuric acid as the anolyte. The cell was successfully used to deposit iron from a 200-600 g/ℓ ferrous sulphate solution at a temperature of between 30-70°C, pH of 2.0-4.5 at a current density of 20-1500 A/m^2. The second patent(178) covers the use of an anion exchange membrane in an electrolytic recovery bath for sulphuric acid pickling solution. Sulphuric acid solution could be continuously recovered from the anode compartment while iron was deposited in the cathodic compartment.

A study of iron electrodeposition from a ferrous sulphate bath using an anion exchange membrane was made by Kondo and Koike(179). They investigated the effects of electrolyte conditions on the efficiency of the electrophysics of ferrous sulphate, and found that a close relationship existed between the concentration of the sulphuric acid in the anolyte and the efficiencies of iron deposition and sulphuric acid generation. An increase in the anolyte sulphuric acid concentration caused a decrease in its generation at the anode, resulting in both the lowering of the pH of the catholyte and the efficiency of iron deposition at the cathode.

Other reports exist on the use of divided cells in the regeneration of ferric chloride etching solutions used in printed circuit board manufacture e.g. Hillis at the Electricity Council Research Centre has worked in this area(180), but discussion of this work would be outside the scope of this review.

(xii) Mechanistic and Kinetic Studies

The subject of the mechanism of electrodeposition of metals and of iron itself has been the topic of many studies, and it was not until about twenty years ago that a real understanding of the field developed.

The development of the theoretical and practical background to the modern interpretation of electrodeposition mechanism has been throughly reviewed and discussed by Bockris and Damjanovic(181). These authors have not only reviewed the development of studies into the mechanism of the deposition of metals in general, but have also provided an excellent treatment on the mechanisms of deposition of iron itself in the same review. Bockris has been one of the leading names in the field of iron deposition mechanism studies having been author and co-author of some of the key papers on the electrode kinetics of iron deposition and dissolution e.g.(182). For a detailed description of his and others' contributions to the field the aforementioned review should be consulted(181).

A limited number of studies have been carried out since the publication of the Bockris and Damjanovic review. Hilbert et al(183-185) have studied the iron deposition reaction from acid solutions under steady-state and nonsteady-state conditions. In the first of these studies(185) a rotating gold disc electrode was used in a 0.1 M $FeSO_4$ solution with a sodium sulphate support electrolyte to investigate iron deposition in the region of limiting diffusion currents and to determine the diffusion coefficient of the ferrous ions. Similar experimental techniques were employed by the same workers to examine the influence of the surface pH on the mechanism of the iron deposition reaction. They found that two different reaction mechanisms were indicated depending upon whether the pH was more or less than 2.8, and that this difference was probably related to the formation of hydrolysis products. Calculation of exchange current densities of the Fe/Fe^{2+} electrode showed that a non-catalysed mechanism was the normal one, i.e. the reaction taking place at $pH < 2.8$. Further studies by the group(185) using rotating platinum disc equipment essentially confirmed their earlier work, but indicated that a pH of 3.3 was the critical value for the changeover of mechanism.

Kinetic studies(186) carried out in an almost neutral electrolyte ($pH \sim 6$) yielded Tafel data which indicated that during Fe^{2+} reduction the two electrons were added simultaneously and allowed an estimation of the exchange current density of iron ($\sim 10^{-5}$ A/cm^2) to be made.

The research described by Bockris and Damjanovic(181) and the papers mentioned above have been concerned with the establishment of basic kinetic and mechanistic data in 'near-ideal' iron electrolytes. It would be unrealistic to expect to obtain this type of fundamental data from concentrated practical plating electrolytes where many more variables are involved, therefore the work carried out on these electrolytes has been mostly concerned with rather empirical definitions of the electrolyte involved and the information obtained cannot necessarily be extrapolated to other electrolytes. Publications in this category include a study of convective streams in highly concentrated solutions of iron chlorides(187), in which the factors effecting these streams such as concentration, temperature viscosity and interelectrode spacing were examined. This study, of course, only applies to unagitated electrolytes where convection plays the major role in metal ion transport.

Studies of cathodic processes occurring in concentrated iron chloride electrolytes have been carried out by Melkov and Namakonov(188,189). In the first, electrodeposition from a 300 g/ℓ $FeCl_2.4H_2O$ bath at 75°C was examined using polarization techniques. A mechanism of the electrodeposition at the pH of 0.5 is postulated, but no further major conclusions were drawn. In the second paper(189) similar work was carried out using the same chloride electrolytes with the addition to the polarization data recorded, the buffer capacity of the electrolyte was investigated and the current efficiency determined. This parameter was found to decrease with the addition of aluminium chloride by some 6-8% owing to increased hydrogen evolution. This has significant implications if the addition of aluminium chloride to working electrolytes is being considered, as a reduction in current efficiency of that degree would be seriously detrimental to the economics of the process.

(xiii) Iron Electrodeposition with Periodic Current Reversal

Many claims have been made that periodic reversal (PR) or interruption or the superimposition of an alternating current onto the direct current supply, can have a beneficial effect on the iron electrodeposition process. Like many other areas of iron electrodeposition research, the work done in this field has largely been empirical and has to some degree been contradictory. No attempt to apply these techniques was made during the course of this project as the field is so extensive that it would warrant long term investigation to reach significant conclusions. However, it was considered that some indication should be given in this review of the nature of the work completed in this area.

The first reports of the application of periodic reverse techniques to iron electrodeposition were made in the late fifties(190 ,191). The major claims of these investigations were that smoother and brighter deposits could be obtained without noticeable effects on the current efficiency on hardness of the deposit. Further claims have been made that the use of the technique resulted in improved structure(192), altered grain size(193) and generally removed any tendency towards anisotropic mechanical properties in the deposit(194).

Related to claims that PR techniques resulted in improved structure are a number of publications(195-198) which indicated that the hardness was increased and the wear resistance of the deposits were improved by its use. The latter of the above publications(198) also investigated the effects of varying the ratio of the total current to the anodic current on the hardness of the deposit. They found that an increase in this ratio increased the hardness of the deposit.

Studies of the effects of PR on the internal stress of iron deposits(199,200) appear to indicate that it was possible to control the magnitude of the residual stresses in iron electrodeposits. A mathematical model was developed(199) describing, simultaneously, the cathodic and anodic current densities, temperature and pulse period effects on the magnitude of the stresses as a function of the thickness of the electrodeposit. The second paper describing the effects of PR on stress(200), was concerned only with a cold iron chloride electrolyte, and the effects of a superimposed assymetric alternating current on deposit properties. In addition to claiming reduced internal stress, this paper also claimed that the deposit adhesion to its substrate was increased and that a deposit with greater wear resistance was produced.

Many of the investigations have included determinations of the current efficiency for the electrodeposition of iron with some form of alternating current control. Work on a cold chloride electrolyte(201) indicated that under optimum plating conditions, the current efficiency was 49-52%. It is interesting to note that the same paper claimed that a many fold increase was possible in the operating current density with the use of an assymetric alternating current compared with cold plating with direct current. Further studies of the current efficiency using PR techniques in cold ferrous chloride electrolyte have been conducted by Bratishchev(202,203), with similar results to the above.

Liskovets(204) has published an interesting report on the effects of the ratio between cathodic and anodic current components on the parameters of iron electrodeposition from a hot (75^{o}C) concentrated iron chloride electrolyte in a flow-type situation. Results indicated that an increase in the above ratio increased the current efficiency, the deposition rate and the microhardness of the deposits.

Finally, recent work by Apetenok and Jansons(205) would appear to increase the evidence that periodic reverse techniques can yield many improvements in iron deposition. Their work indicated that the rate of deposition could be increased, the physical properties of the deposit improved and the adherence of the deposit to the substrate improved, by the use of this technique.

(xiv) Final Comments

The electrodeposition of iron alloys (binary and ternary) is a large and significant field, for which there is a large literature. This field is, however, outside the scope of this review and for present purposes has not been considered.

The history of iron electrodeposition as can be seen is long and detailed, and to a large degree empirical in nature. No single review could claim to be completely comprehensive in providing an insight into the field because of its extent and the necessarily unco-ordinated manner in which most of the work has been conducted. It should also be noted that some information is unavoidable because, as is often the case in applied technology, some research will have been done by private and industrial concerns, which has not appeared in the scientific and technical literature.

III PATENT REVIEW

DEVELOPMENT OF CONTINUOUS FOIL ELECTROFORMING TECHNOLOGY

The patent history of continuous foil electroforming can be traced back to a 1933 patent by the Anaconda Sales Co. U.S.A.(206). It concerned the electroforming of an endless foil (particularly copper) followed by reinforcement in a second bath to give it the required thickness. The patent covered many years of research and development resulting in the commercial operation of a lead covered copper drum mounted horizontally on a lead lined concrete tank so that it was partly immersed in the electrolyte, (Fig. 3.1). The cylindrical surface of the drum immersed in the electrolyte was opposed by lead anodes spaced about 1cm from it. Violent air agitation supported the stirring effect of electrode gassing in the bath. In the second, reinforcing, vat the foil was led concertina-like vertically up and down over a number of rollers, one being near the tank bottom and the next one just below the electrolyte surface. Within each of these vertical folds a row of anodes was suspended from a bar across the vat.

Lead was found to be the most suitable metal for the cathode given the corrosive nature of the acid copper electrolyte. To maintain a satisfactory finish on the foil the cathode surface was continuously abraded and polished during operation.

Further consideration of the cathode surface material was made by Wynne-Williams in his 1934 patent(207). In it he suggested the use of a chromium or chromium plated cathode surface. The use of such a cathode surface was claimed to overcome the problems of formation of a cathode film and adhesion problems found on previous rotating cathode mandrels. The specification also provided for the use of one or more skimming members which act on the cathode to reduce to a minimum the thickness of the cathode film.

In a patent specification(203) issued at about the same time as the Wynne-Williams specification, the Anaconda Copper Mining Co., described a refinement to their continuous foil electroforming cell in which they claimed to have overcome the difficulty of providing satisfactory edge delineation particularly on thinner gauge foil.

The problem of obtaining a foil with sharp clean cut edges and preventing deposition or dendritic growth on those surfaces of the drum where it is not desired was one of the most important obstacles to commercial production.

Previous attempts to overcome these difficulties included application of an insulating coating to the curved surface of the drum at its ends, or to apply a gasket or disc of insulating material to the ends of the drum. While these expedients may function satisfactorily for some time they do not provide a permanent solution to the problem.

The solution suggested by Anaconda is a combination of mechanical and electrical means. Increased thickness at the edges of the sheet was prevented by means of shields that obstructed the flow of current from the edges and back of the anode. A clean-cut edge, which may be stripped without tearing was produced by secondary cathodes suspended on the tank walls, so connected that they were cathodic to the ends of the drum. The solution at the ends of the drum was separated from the main body of the electrolyte by means of the shields referred to. The surface of the ends of the drum was always anodic to the electrolyte in contact with it, and no plating on it was possible, while the cylindrical surface of the drum on which the sheet was deposited was cathodic to the main body of the electrolyte.

A further refinement in the electroforming and handling of foil is covered in an Anaconda patent of 1941(209). Stripping thin foil from the cathode had continued to be a problem because of the ease with which the foil tears at the edges. A tear not only spoilt the product but caused serious delays in production. The new method for foil removal described in this patent involved separatingthe centre portion of the foil in advance of the edge portions from the cathode. Thus, the minimum of stripping strain was put on the edges and the development of edge tears minimised. The essential feature of the mechanism described in this patent for removing the foil in the desired manner was a tapered roller mounted for rotation about its longitudinal axis in close proximity and parallel to the cathode surface, with its centre section of greatest diameter over the centre section of the drum. The apparatus is shown in Fig. 3.2.

The rapid development of the electronics industry in the post Second World War period created a large new market for electroformed foil, particularly copper, for the manufacture of printed circuit boards. A Ferranti patent(210) linked copper foil electroforming with printed circuits and other electrical uses calling for the bonding of such foil to phenolic/paper laminates. The patent aimed at electroforming foil one side of which was particularly rough. This was in order to increase the bond strength with the laminate at the interface. Copper from an acid bath was, initially, deposited at about 1100 A/m^2 with bath agitation. Then the foil was rinsed and transferred to a cyanide bath of the same deposition speed at half the current density but without agitation, thus producing the required roughness. The patent protected both acid/alkali foil as described above as well as giving existing foil a rough and hence adhesive surface by unagitated alkaline deposition. In the latter case the patent specified an intermediate layer of freshly deposited copper in order to improve adhesion and cohesion.

In an effort to improve foil quality and plant operating conditions the Anaconda Co., patented a method of delivering the electrolyte continuously into the space between the cathode drum and the anode(211,212). The 1933 patent(206) showed the necessity for agitation (most conveniently air) to produce sheet having a high degree of uniformity of gauge and freedom from pinholes. However, air agitation proved to be objectionable on a number of grounds. It produced an irritating acid mist requiring workmen to use respirators and causing discolouration and corrosion to occur on the electrodeposited sheet. Splashing of the electrolyte near the cathode drum also resulted in wetting and trapping of lead dust (generated by the cathode polishing apparatus) on the surface of the drum leading to defects in the deposited sheet.

The improved apparatus is shown in Fig. 3.3. As can be seen, the major development was the introduction of a pressurised electrolyte inlet manifold located below the bottom of the cathode drum. The electrolyte was pumped upwards and circulated around the drum in turbulent motion resulting, it was claimed, in an electrodeposited foil of exceptional uniformity and remarkably free of pinholes and other porosity, even down to average gauge thicknesses of little over 0.001 in.

As a result of U.S. Government specifications requiring a non-porous copper foil of at least 99.5% purity for printed circuits, the the Clevite Corp obtained patents(213,214) for an improved method of electroforming thin copper foil. The method utilised a chromium plated drum similar to the Wynne-Williams patent(207), the improvement being in the method of preparation and care of the chromium plated surface. The patent covered the preparation of a stainless steel or regular steel drum, followed by the application of a special crack-free layer of chromium and the preparation of this surface to remove oxides and chromium complexes. The drum was then quickly put into service, almost completely immersed in the electrolyte and immediately covered with a thick pore free layer of copper, to protect the surface from oxidation and/or contamination. This copper layer was removed just prior to the continuous plating operation.

Continuing the association of electroformed foil with the electronics industry, Conley, Turk and Pochapsky obtained a patent(215) in 1965 for a claimed improvement in nodularised copper foil for printed circuit boards. Plating conditions and electrolyte content were defined to give a foil with the appropriate surface finish for optimum adhesion to the circuit board laminate.

A possible alternative to the rotating drum electrode was proposed by Pedone in a British Patent of 1967(216). This invention consisted of a cathode made of an endless tape wound around rotating devices. The tape was made at least partly of electroconductive material such as stainless steel and partly immersed in an electrolyte containing bath with some means of agitation provided. The arrangement is shown in Fig. 3.4.

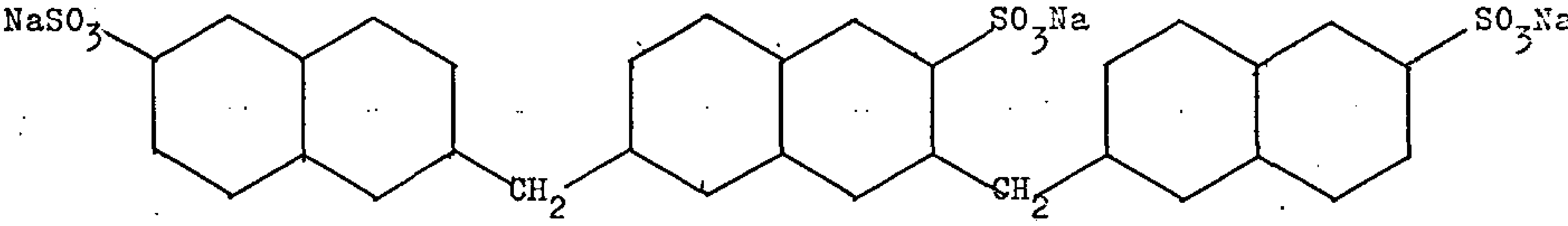
The inventor claimed some advantages for the method. The cathode tape can be made any length allowing plating over a large area, considerably increasing the output of the apparatus as well as the efficiency of production. A cathode cylinder of considerable dimensions would be necessary in order to reach high production rates. The endless belt cathode facilitates the use of soluble anodes unlike the rotating cylinder where the anodes must maintain close proximity to the curved surface of the cylinder.

In 1967/68 General Motors patent specifications(217,218) published in Britain and the U.S.A. relating to the use of a ferric hydroxide dispersant in iron plating baths. Although not intended primarily for use in continuous iron foil production, the principle was eminently applicable to this field where quantities of this particulate contaminant will be formed both by atmospheric oxidation and as a by-product of the electrolysis process.

The patent covered the use of an additive of a water soluble salt of a condensation product of a β-napthalene monosulphonic acid and formaldehyde which has the following formulae:

$$C_{10}H_6\ SO_3Na - CH_2 - C_{10}H_6SO_3Na - CH_2 - C_{10}H_6\ SO_3Na$$

The structural formula is:



This was added to a ferrous chloride bath in quantities of between 0.25 and 1.0 grams per litre of electrolyte. The specification claimed that this dispersant allowed the electrodeposition of substantially smooth and pit free layers of iron without the use of filters which were prone to clogging. It was also claimed that anode efficiency could be improved since it too will be adversely affected by ferric hydroxide fouling.

A British patent(219) taken out by a Bulgarian Corporate Body sought to provide a method of electroforming metal foil at current densities much higher than previously possible. They claimed that previous methods allowed deposition with current densities from 800 to 2000 A/m^2 whereas with their apparatus current densities of up to 6000 A/m^2 were possible. The former methods were limited at high current densities by ion migration, diffusion and convection limitations, because of insufficient agitation. The specification provided for the familiar rotating cylindrical cathode concentrically opposed by a semi cylindrical anode. The improvement lay in the delivery of the electrolyte under pressure to the anode cathode gap from the bottom of the anode. The arrangement was such that a continuously changing stream of electrolyte could be supplied to the gap over the full width of the drum. This stream of electrolyte reduced the thickness of the cathode diffusion layer to a minimum and thus permitted the application of high current densities. A schematic diagram of the cell is given in Fig. 3.5. The ideas covered in this patent appear to be very similar to those detailed in Anaconda patents of 1958(211) and 1959(212) and differ only in minor detail.

A significant advance to electroforming technology was made in an Anaconda Co., patent(220) of 1969. This patent provided for the use of a titanium clad rotating cylinder cathode. The lead covered drums proved to have a number of inherent disadvantages. For example, the oxide formed on the cathode surface during the plating process had to be removed continuously by grinding and polishing, increasing the labour requirements and wearing down the drum surface, leading to periodic resurfacing requirements. Moreover, lead particles caused contamination of the foil. The use of stainless steel as a cathode drum surface required a special electrolyte solution and operated at a comparatively low temperature not exceeding ∿ 40°C. Successful plating on the chrome plated drums was very dependent on the chrome surface. Special preparation and frequent maintenance of the chrome surface was of extreme importance. The increased maintenance led to increased costs and lack of competitiveness in the production of commercial grade foils.

The specification claimed that it was possible to produce high grade copper foil by electrodeposition on a drum made by engaging the inner surface of a titanium cylinder which has a non-porous and smooth outer surface with a mating surface of an electrically conductive metallic structure. (See Figs 3.6-3.7). The importance of good physical contact between the titanium shell and its metallic support was emphasised as was the requirement for a thin shell of titanium rather than a solid titanium cylinder because of the metals' relatively low electrical conductivity. Since titanium forms a smooth and tenacious oxide coating, grinding and polishing were no longer required. Additional cost savings were made from the fact that the plating temperature of conventional copper plating baths could be elevated to between 50°C-60°C.

In the early seventies a number of patents were issued covering the continuing development of copper foil specifically for the electronics industry. The Circuit Foil

Corporation devised methods (221,222) for making copper foil with improved bond strength between the foil and the laminate especially at high temperatures. This was achieved by coating the matt side of the foil with a metal which at elevated temperatures was substantially inert to the substrate e.g. nickel. Patents were issued to the Clevite Corporation (223,224), protecting methods for the prevention of foil staining on printed circuit boards. This again was done by electrodeposition of various metals on to the copper foil.

At about the same time as the above, Circuit Foil obtained patents in the U.S.A. (225) and Britain (226) for improvements in foil electroplating techniques in which a continuously moving sheet was moved in a serpentine fashion into and out of an electrolyte between successive planar anodes (Fig. 3.8). The improvements related to overcoming problems concerned with current distribution over the plating surface due to ionic imbalance in the electrolyte bath which in turn could be related to variations in the degree of flow and agitation in the bath during electrodeposition. The essence of the patent lay in confining the electrolyte between the cathodic sheet and the anode to prevent transverse migration of electrolyte across the strip. The gas evolution which took place between the strip and the anode then created an air lift effect which acts as the driving force for a pumping system which carried the electrolyte up over the tops of the anodes giving an almost uniform circulating pattern.

The beginning of the last decade also saw the first of a number of patents relating to the continuous electroforming of iron foil. In October 1971 a patent(227) was taken out by the British Iron and Steel Research Association covering the application of continuous foil electroforming technology to the production of iron foil. The patent specified the use of an 'endless moving matrix' as cathode to produce the thin strip which was then moved between porous planar anodes in a second bath so that its thickness can be increased as required. The use of iron chloride and iron sulphate electrolytes and the possible use of iron ore or scrap iron based electrolytes was covered. The conditions for plating were defined as was the use of graphite anodes capable of withstanding the demanding conditions of a hot, acidic bath.

Approximately two years later, the Electricity Council patented(228,229) an apparently improved method of iron foil electroforming, essentially consisting of a rotating cathode cylinder with a titanium surface partly surrounded by a closely spaced anode of insoluble material. The apparatus included a method for heating the cathode cylinder to maintain it at a uniform temperature greater than that of the electrolyte so that the foil would not have non-uniform characteristics due to temperature variation. Apart from these modifications the patent appears to be similar to that of the British Iron and Steel Research Association(227).

The Electricity Council were also working on the idea of using tin cans and tinplate off-cuts as a source of iron for iron foil electroforming. They patented(230) a method which included the step of recirculating used electrolyte over metallic iron where at least part of the iron was in the form of tin plated iron. They claimed that the tin ions spontaneously precipitate out forming a sludge in the ferrous chloride electrolyte. Where the tin ions do not precipitate out spontaneously, they proposed the addition of a selective chelating agent to effect precipitation. In cases where lead may be present (from lead solder used in the assembly of tin cans), the patent proposed the use of another chelating agent. The actual chelating agents used were not specified in the patent. It was suggested that the tin and lead may be recovered by suitable processing of the sludge.

The Continental Can Co., were also working on the iron electrofroming electrolyte. In a patent(231) published in October 1975, they proposed a novel method for counteracting the build-up of solid ferric chloride during continuous iron electrodeposition. The process, which may be applied to many solid/liquid reactions, involved passing the solid reactant (e.g. ferric hydroxide) into a rapidly rotating cylinder which has porous walls. Centrifugal force caused the solid to be propelled against the walls of the chamber. The chamber was then charged with the second reactant (e.g. hydrochloric acid) which was propelled into the solid lining the walls. During its passage through the solid particulate layer, chemical reactions take place and the reaction product is expelled through the openings in the wall.

An improvement to the method of electrodepositing a metal onto a moving foil cathode was patented by the Electricity Council in December 1975(232). The major modification was located in the secondary cell where further metal was deposited onto a foil, made on an endless matrix in the primary cell. It concerned the distribution of large currents through a thin foil of, for example, 0.001 inch thickness. In previous systems the foil was coupled to the current scource by means of rollers and with the large currents involved over a relatively small area of contact, problems such as burning and uneven current density occurred. This patent sought to avoid this by using a large area of contact. As shown in Fig. 3.9, the foil is drawn over a conducting support which contacted essentially the whole area of the foil to be plated. In this way the current passed through the foil substantially perpendicular to its plane and was very uniform.

A new approach to carbon anode construction was patented (233) by the Electricity Council in 1976. Again the object was to improve uniformity of the electrolysing current. It had been shown that large conforming anodes formed from a block of graphite sometimes displayed non-uniform current distribution characteristics. This was due to the resistivity of the graphite and the length of the current flow paths from the point of connection with the current scource to the anode surface. The proposed solution consisted of constructing an anode by attaching graphite strips with a non-degradable, conductive adhesive onto a conductive metallic surface shaped appropriately as the abode. In use, the metallic conductive portion was connected to the current scource. The current could then flow to all parts of the anode surface with no appreciable drop in potential, hence all of the working area of the anode was at substantially the same potential and the current density constant.

One of the more recently published patents in the continuous foil electroforming field is one from Gould Inc.(234). The invention concerned an improved method of electrodepositing iron foil on a rotating drum cathode in conjunction with a soluble anode made of iron or an iron containing material. The arrangement is shown in Fig. 3.10. The operation was similar to the rotating cylinder cathode devices described previously except that the anode was arranged so that it could be moved nearer to the cathode surface as it was consumed. It was claimed that this method of foil production produced foil which was less prone to suffering from hydrogen embrittlement as a rather less acidic electrolyte could be used, and in addition, higher current densities could be used.

A patent(235) filed in Britain in December 1975 and published in 1978 considered another approach to the possibility of using consumable or semiconsumable anode materials. In this case the rotating drum cathode was half surrounded by a melded fibre belt which was in turn surrounded by the consumable anode material. The belt ensured a constant gap width and was fixed in position relative to the anode material. The rotation of the cathode relative to the melded fibre caused the fabrics to act on the surface of the electrodeposit to break up the depleted barrier layer. The layout of the apparatus is shown in Fig. 3.11.

The arrangement described above should not be confused with the idea patented by Eisner of the Norton Co.,(236) where the cathode was continuously activated by a moving belt of small, hard, spaced particles supported by a matrix, apparently permitting very high current densities and deposition rate. (Some doubts have since been expressed about the validity of the claims made by the Eisner patent).

In conclusion, the development of continuously electroformed foil technology has been traced through the patents, from its origins in the copper foil industry to the present day where the technology finds application in many areas. Iron foil can be seen as a logical development and application of knowledge gained from the copper foil industry. Nickel foil in various forms is an important industry. It is, however, largely non-patented being based on know-how and novel application from the aforementioned areas.

IV. IRON FOIL PRODUCTION ON A PILOT PLANT

(i) Introduction

The work described in this chapter resulted from the operation of a pilot-scale plant for the continuous production of iron foil from a concentrated ferrous chloride electrolyte.

The plant was situated at the British Steel Corporation Research Laboratories (Swansea). Its origins can be traced directly to the work carried out by Brown and Salt at the British Iron and Steel Research Association's Laboratories, later disclosed in patent form(227), and described in Chapter III of this thesis.

The pilot plant had been in use for a number of years and contributed to the B.S.C.'s fund of knowledge of iron foil production. It became available for use during this project as a result of a co-operative development agreement between the B.S.C. and the Arthur Lee Group.

The objectives of the work were to attempt to gain some insight into the operation of this type of plant, that could later enable better judgement to be made on the implementation of ideas arising from laboratory work, and to try to obtain a more detailed understanding of the processes involved in the practical plating operation.

The general layout of the plant is shown schematically in Fig. 4.1, and a full description of the plant follows.

(ii) Plant Description

Electrolyte

The electrolyte was prepared by dissolution of scrap black plate in commercial grade hydrochloric acid and mains-supply water. The iron concentration was monitored by conventional titration against N/2 potassium dichromate(237) using barium diphenylamine sulphonate as indicator. Hydrochloric acid was added to the system until the concentration of the ferrous chloride reached ~3 M. The pH of the solution, prior to starting plating, had to be kept above zero to avoid excessive damage to the cathode and below 4 to avoid brittle foil.

Electrolytic Cell

The cell consisted of a rectangular container with a 24 litre capacity. It was constructed from 10 mm Tufnol sheet. The electrolyte entered the cell from the top over a weir to ensure constant level, and was removed from the cell via a drain in the cell floor and via an outlet at the level of the weir to prevent overflow. The rate of flow through the inlet and outlets could be controlled by simple valves.

The cathode was mounted horizontally in the end walls of the cell by liquid-tight bearing seals. The cathode consisted of a machined cylinder of solid titanium, drilled to reduce its weight. Both ends of the cathode were sealed off with discs of Tufnel to prevent overplating. The working width of the cathode was 14.6 cm. The edges of the deposition area were delineated with 'Silastomer' silicon compound.

The anode was machined from graphite block and contoured to be concentric with the cylindrical cathode surface. The anode-cathode spacing was 0.8 cm. The anode covered an arc of 15.5 cm giving a working area of 226 cm^2.

The current was supplied to the cathode via three copper brushes acting on a phosphor-bronze slip ring. The anode was supplied from the bus bars via 'Karbate' anode inserts.

Electrolyte Regeneration System

The regenerator consisted of a covered rectangular polypropylene container of approximately 275 litres capacity. This was divided into three equal parts by two weirs to direct the spent electrolyte through the scrap black plate.

Baskets made of titanium mesh on a titanium frame were used to contain the scrap in the regenerator. Eight (1 kW) titanium clad heating elements were used to heat the electrolyte to the required temperature. The temperature control was by means of two mercury contact thermometers switching the heaters via 'Gallenkamp' 20 A relays.

Pump and Header Tank

The electrolyte was circulated by a ¾" Jabsco pump fitted with a neoprene impeller on a titanium shaft. A constant solution head was provided for the pump by a 30 ℓ polypropylene header tank mounted slightly above the level of the pump.

Storage Tank

The system was provided with a large polypropylene storage tank (capacity > 1000 ℓ) for the storage of surplus electrolyte and for removing the electrolyte from the scrap when regeneration was not required. Use of the storage tank required an extra pump fitted with flexible hose, hence the electrolyte could only be pumped to the storage tank when it was relatively cool (< 80°C) otherwise the flexible tubing collapsed.

Connections

The components of the plant were interconnected with 1½" high density polypropelyne tubing supported on slotted angle frame. Polypropylene tubing provided the desirable combination of durability and ease of assembly.

Power Supply

The direct current required for the plant was supplied by a 'Westinghouse' 500 A, 16V mains rectifier operating from a 400 V 3-phase supply. The rectifier was equipped with a Westinghouse thyristor central unit. The current was measured using a 'Fluke' digital multimeter across a 0.0015 Ω shunt.

The rectifier was somewhat dated and produced a rather spiky waveform which will have introduced some degree of inaccuracy. Also, the rectifier was not able to provide a current lower than about 60 A. For currents lower than this a 30 A battery charger was used.

Foil Post-Treatment

The iron foil produced was continuously peeled from the cathode drum, it was then rinsed on both surfaces by mains water from a sprinkler system. The rinsed foil was then drawn through a citric acid bath at 50°C and then rinsed again. The foil was then dried by means of a hot air blower, treated with WD40, coiled and stored in sealed plastic bags until examination.

Instrumentation

The cathodic polarization data were obtained using a 'Vibron' Electrometer Model 33 B-2. The potentials were measured against a saturated calomel electrode. The electrode was not placed directly into the solution to avoid contamination, but via a KCl salt bridge and Luggin probe with a ceramic tip.

All values of pH were measured by sampling and using an 'EIL' Model 31 pH meter (± 0.1 pH) with automatic temperature compensation. The pH electrode was an 'Activon Glass Ltd.,' high temperature model for use above 50°C.

Conductivity values were obtained using a 'Philips' Model PW 9501 conductivity bridge employing a 'Philips' Model

PW 9517 conductivity cell with a cell constant of 28.3 cm^{-1}. A 'Muirhead' decade resistance box was used in conjunction with the conductivity meter to expand its working range.

(iii) Experimental

Start-up Procedure

A strict routine had to be followed in order to start production of satisfactory foil. To start a production run, the electrolyte was drained from the storage tank into the regeneration and header tanks. Once the electrolyte had reached a suitable height in the header tank, the pump could be switched on and the electrolyte circulated around a closed loop through the pump, regenerator tank and header tank. The cell was not included in the circulation loop at this stage so that the cathode would not be damaged by the electrolyte if its pH happened to be too low.

Once the electrolyte was circulating the heaters could be switched on. When the temperature had risen to more than 50°C, samples of the electrolyte were taken and tested for pH and concentration. Adjustment of these parameters was made if necessary by addition of water and/or concentrated hydrochloric acid until the pH was in the region of 1-2 and the concentration was about 3.0 M.

When the electrolyte temperature had reached about 100°C it was circulated through the cell and a few minutes allowed for the cell and electrolyte to reach operating temperature.

With the cathode drum stationary, the current was switched on and adjusted to about 4000 A/m^{-2}. Approximately 3-4 minutes were allowed for deposition of an adequate layer of foil. The cathode was then rotated with a peripheral velocity of 5 $cm.min^{-1}$, giving a foil thickness of just over 50 μm. The leading edge of the foil was peeled off the cathode surface using a scalpel blade and drawn over rollers and fed into the wash and citric acid baths. After treatment and drying under a hot air blower the foil was coiled on a cardboard roll, the appropriate tension being applied by an electric motor via a magnetic clutch.

During a run, the edges of the foil, as it came off the cathode, had to be examined regularly as they were rather prone to tearing. This fault was more noticeable as the foil was made thinner.

Starting Conditions

It was important to keep the starting conditions in the region mentioned above i.e. pH of 1-2, concentration ∿ 3.0 M, temperature ∿ 100°C, and initial take-off speed of 5 $cm.min^{-1}$. Failure to keep the first two parameters within the said limits resulted in hard, brittle foil which was extremely difficult to remove from the cathode surface. Other factors may have been important at this stage e.g. Fe (III) concentration, but further work was needed to examine this. Once the foil was leaving the cathode surface cleanly, the current density and/or drum rotation speed could be adjusted as required.

Shut Down Procedure

The power supply was shut off and the end of the foil removed from the drum ensuring that no small pieces of foil were left on the drum. The cell was then drained and the electrolyte allowed to cool to less than 80°C before it could be pumped from the regenerator to the storage tank. The solution could not be pumped into the storage tank while still hot because a portable Jabsco ½" pump with flexible tubing had to be used and the tubing collapsed if the temperature was greater than about 80°C.

Polarization Studies

Galvanostatic polarization data were obtained from two production runs. They were obtained, beginning at the normal start up current density of about 4000 Am^{-2}, increasing the current density manually to over 6000 Am^{-2} then reducing it to as small a value as the apparatus would permit. Approximately five minutes were allowed after each change in current density for the system to equilibrate.

There was significant fluctuation in the 'Vibron' reading and thus the results shown can be considered only as the median value.

Values of the cell voltage were also obtained from one of the runs.

pH Studies

Variation within System: The pH of the cell was monitored by sampling from the major components of the system i.e. the cell, the regenerator and the pump header tank.

Variation with Time: The pH of the cell was monitored during a number of foil production runs from the start up to shut down. The results obtained give a clear indication of the trend of the pH during a run.

This procedure was carried out during runs with continuous regeneration of the electrolyte and repeated for runs without regeneration.

Conductivity Measurement

Values of the conductivity of the electrolyte were obtained by monitoring the electrolyte in the cell directly during the plating operation.

Cathode Current Efficiency

The efficiency of the foil production from a typical solution was determined using as long a production run as possible to maximise accuracy. The procedure involved ensuring as constant a current as possible during the run and then accurately weighing the foil produced in a given time, at a known current.

Ferric Ion Concentration Studies

The method used for the determination of the ferric ion concentration was by titration against potassium dichromate.

The method involved a determination by difference i.e. the ferrous ion concentration was determined, and the ferric ion then reduced to ferrous by addition of stannous chloride. The total iron concentration could then be determined. The ferric iron concentration was the difference between the two determinations.

Samples of electrolyte were taken from the cell during normal operation at given time intervals and the determinations made as quickly as possible.

(iv) Results

Figure 4.2 shows the galvanostatic polarization data corresponding to typical plant operation. An indication of the accuracy of the measurements is given on the graph. Figure 4.3 shows the cell voltage during a typical polarization. run.

The pH determinations within the different parts of the system showed no detectable differences during normal operation.

Figures 4.4-4.5 show the trend of pH with time under normal operating conditions with the electrolyte undergoing continuous regeneration. It can be seen that the pH dropped rapidly in the first 10-15 minutes of operation after which it steadied out on a constant value. The results obtained without continuous regeneration of electrolyte showed a similar trend.

The conductivity of a typical electrolyte was found to show no detectable change with time during the plating operation. This can be seen in Fig. 4.6. The value of the conductivity under the conditions given on the figure was found to be 0.34 Ω^{-1} cm^{-1}.

The cathodic current efficiency for foil production from a typical solution was found to be 91.3%. The electrolyte was 2.95 M in ferrous ion with an average pH of 1.5 at a temperature of 98.6°C.

The study of ferric ion concentration showed that under normal plating conditions with continuous regeneration and recirculation of the electrolyte the concentration of the ferric ion did not rise above about 1% of the total iron concentration and in fact may have been rather lower than this, as 1% is about the limit of accuracy of this method of determination.

Confirmation of this was provided by prolonged running without regeneration to allow a build up of ferric ion concentration. This showed that even after five hours of plating the ferric ion concentration had only risen to about 0.03 M or 1% of the total iron concentration.

A further result from the work on the pilot plant arose from the examination of the black particulate scum that was observed on the surface of the electrolyte after prolonged dissolution of scrap. A sample of the material was collected and warmed with an excess of concentrated hydrochloric acid. Little dissolution was observed indicating that the material was not magnetic and was possibly particular carbon.

(v) Conclusions

(a) The polarization data obtained was limited in extent because of the plant limitations at the low current end of the scale. They do, however, show that there is no trend towards a limiting current density even at current densities well above the normal operating values. This was later confirmed by laboratory studies.

The degree of polarization of the system compares favourably with results obtained in the laboratory, indicating that the laboratory data should be applicable to plant operation at this scale.

As mentioned above, no information could be obtained about the effects of Fe^{3+}/Fe^{2+} reduction in this system as it could not be operated at low current densities.

(b) The lack of variation within the system establishes that the regeneration and circulation capacities were adequate for the system.

The rapid change in the pH of the system at the start of the deposition process indicates that a new set of equilibrium conditions are set up when the current is switched on.

(c) The value of electrolyte conductivity agrees generally with those found under laboratory conditions.

(d) The determination of the cathode current efficiency for the deposition of iron confirmed results obtained by British Steel and Arthur Lee on other plant that the current efficiency lies between 90 - 95% for a typical working electrolyte. The value obtained (91%) is rather lower than values obtained under laboratory conditions which is probably due to the greater concentration of Fe(III) present in the pilot plant electrolyte than in the laboratory cell where conditions could be more vigorously controlled.

(e) It was hoped that extent of ferric ion generation in the plant could be established. (During operation there was a distinct change in the electrolyte colour from clear green to a colloidal yellow-brown). However, the change in concentration proved to be so small, that it would only be possible to state that under normal operating conditions the ferric ion concentration does not rise to more than 1% of the total iron concentration. It should be noted that the regeneration side of this plant was originally designed to supply a much larger cell, so it had a very high regenerative capacity.

(f) The black particulate material sometimes present in the electrolyte was probably particular carbon from the carbides present in the scrap.

V. EXPERIMENTAL

1. Conductivity Measurements

Solution Preparation

The test electrolytes were made up in distilled water from 'S.L.R.' quality reagents. (Purity > 99%). The solutions were de-oxygenated with oxygen-free nitrogen, to minimise the effects of atmospheric oxidation of the ferrous ion in solution.

The concentrations of the conductivity salt additions to the solutions were chosen so that the solutions would not be completely saturated at room temperature, as this would obviously be undesirable in both experimental and plant conditions. The background concentration of ferrous chloride in each solution is 1.5M.

The electrolyte sample size was 100 cm^3; this was made up in Grade A Standard Flasks to within ± 0.08 cm^3. All weighings were carried out on a 'Mettler P1210' balance with an accuracy of ± 0.02g.

The pH of all of the solution was adjusted to 0.00 ± 0.05 with hydrochloric acid using a 'Corning-Eel' Model 12 pH meter in conjunction with a 'Corning' 476050 Semi-Micro Combination pH electrode with an internal silver/silver chloride reference.

Conductivity Cell

The conductivity cell is shown in Fig. 5.1. The cell was a commercially produced model (Philips P.W. 9517 Immersion) and had a pre-calibrated cell constant of 28.3 cm^{-1}. It was constructed from 'Pyrex' glass with cylindrical platinum electrodes, and could be operated with a minimum sample size of 4 cm^3 over a range of 1-1000 $m\Omega^{-1}$ cm^{-1}.

Conductivity Meter

The conductivity meter used was a direct reading Philips Laboratory Conductivity Meter P.W. 9501/01. Figure 5.2 is a schematic illustration of the basic components of the meter. Measurements were made using an audio frequency (2000 Hz) alternating current in order to minimise polarization errors. (200 Hz) was also available with the instrument). As shown in the diagram the a.c. is generated by an oscillator linked to on a.c. impedance bridge, one arm of which is formed by the cell. In the meter the variable impedance arm and the detector are linked to give a direct read-out, and the facility to adjust the other arms of the bridge is provided to allow cell constants of between 0.01 - 30 cm^{-1} to be used.

Procedure

Aliquots of approximately 25 cm^3 of the test solution were contained in modified boiling tubes suspended in a 25 ℓ water bath, thermostatically controlled to within ± 0.1°C by a 'Tecam' thermostat/stirrer. A 'Red rod' silica sheathed heating element was used as an auxiliary heater at the higher temperatures. The tubes were sealed with rubber bungs to prevent evaporation losses at higher temperatures and to minimise atmospheric oxidation.

The conductivity of each solution was then determined at the temperatures indicated by immersing the conductivity cell into the test solutions, ensuring that the system came to thermal equilibrium in each case.

A background conductivity determination was carried out to determine the contribution of the make-up distilled water to the overall conductivity. This was found to be less than $10^{-5}\Omega^{-1}$ cm^{-1} in each case and was thus negligible in comparison with the overall conductivity (between $0.2 - 0.6\Omega^{-1}$ cm^{-1}) of the test solutions.

2. Polarization and Laboratory Cell Work

(i) Initial Polarization Studies

Preparation and Pretreatment of Planar Titanium Cathode

The initial polarization studies were carried out using a 1 cm^2 planar titanium electrode. Various methods of sheathing the titanium to produce a 1 cm^2 surface were tested. These were ranged from simply masking a 1 cm wide strip of titanium with P.T.E.E. tape leaving a 1 cm wide section exposed. This did not prove successful as some iron deposition took place under the edges of the tape. Attempts were then made to sheath a 1 cm x 1 cm x 0.5 cm piece of titanium in silicon rubber compound using a perspex mould to cast the rubber around the electrode. This was unsuccessful as the silicon rubber would not form a satisfactory seal on the edges of the electrode, therefore some deposition could occur on the sides of the titanium. A successful electrode (shown in Fig. 5.3) was finally prepared by setting the titanium electrode in a vinyl ester epoxy resin using the perspex mould mentioned above. The vinyl ester resin was chosen after it was found that 'Araldite' brand epoxy resin could not withstand long term contact with the hot electrolyte.

To prepare the electrode for use, it was ground on progressively finer grades of emery paper. The electrode was then thoroughly degreased in 'Genklene IV' in an ultrasonic bath, and finally rinsed in distilled water.

Preparation of Test Electrolytes

The test electrolytes for this section of the work were prepared in the manner described in Section V.1.(i). Since the electrolyte used (3.5M ferrous chloride) was very near to saturated, great care had to be exercised so that a solution of correct concentration and pH could be prepared.

Counter Electrode

The anode consisted simply of a strip of electrolytic grade graphite (obtained from the British Steel Corporation Research Laboratories in Swansea) partially coated with silicon rubber to minimise absorption of the electrolyte. Its general form is shown in Fig. 5.3, and its dimensions were such that it could be inserted and removed via the neck of the vessel used for the reaction cell.

Reference Electrode System

All the potentials quoted in this thesis were made with reference to a standard saturated calomel electrode (i.e. + 242 mV vs Standard Hydrogen electrode potential at 298 K).

The measurements were made using a commercial 'EIL' Laboratory calomel reference electrode system with an extended ceramic tipped Luggin probe (shown in Fig, 5.4). The tip of the Luggin was placed at the top of the working electrode so that it would not impede the current path between anode and cathode. The ceramic tipped Luggin proved very convenient and effective as it was not prone to leakage nor form bubbles in the probe as is often the case with capillary Luggin probes. Its major disadvantage is that the potential sensing tip is approximately 1 mm away from the electrode surface which can lead to inaccuracy at high currents or in low conductivity solutions. Neither of these conditions arose during this section of the work and the method proved entirely satisfactory.

Electrolytic Cell

The layout of the cell used for the initial polarization studies is illustrated in Fig. 5.4. The basic vessel consisted of a 'Pyrex' 500 ml culture vessel (Quickfit FV 500) with a five necked lit (Quickfit MAF 1/75) clamped together and using a P.T.F.E. gasket to ensure a good seal. The working and counter electrode were inserted through opposite necks of the lid and fitted into a polypropylene spacer at the bottom of the flask to ensure a constant inter-electrode spacing. The Luggin probe of the reference electrode was located through one of the remaining circumferal necks and adjusted so that it was situated near to the top of the working electrode. A nitrogen diffuser fitted through the fourth of these necks. This provided both agitation of the electrolyte and displaced dissolved oxygen from the electrolyte. A reflux condenser and gas jet was fitted to the remaining neck to minimise evaporation losses during operation at elevated temperatures.

Heating and temperature control to $\pm$ 0.1°C was provided by a thermotastically controlled 'Tecam' thermostat/stirrer.

A 'Red rod' silica sheathed heating element was used for auxiliary heating at elevated temperatures.

Potentiostat, Linear Sweep Unit and Ancillary Equipment

The potentiostatically controlled current supply was provided by a 'Chemical Electronics TR 40 (3A)' potentiostat. The potential ramp for the polarization determinations was generated by a 'Chemical Electronics' Linear Sweep Unit connected directly to the potentiostat. This permitted an overpotential of up to 3000 mV on the working electrode.

The cell current was usually measured across an external 1Ω calibrated, non-inductively wound, 'Ni-Chrome' resistor. For larger cell currents, two 1Ω resistors were used in parallel. The potential across the measuring resistor was registered using a 'Vibron' Electrometer Model 33B-2, the output of which was recorded, via a potential divider arrangement of decade resistance boxes, on a 'Bryans 28000' X/t chart recorder.

Electrolytic Cell Circuit

The electrical circuit is shown in Fig. 5.5a. The system consisted of a conventional three electrode arrangement of working, counter and reference electrodes. The potentiostat is essentially an operational amplifier which has the electrochemical cell forming the elements of the feedback loop as shown in Fig. 5.5a. The reference electrode is kept at the vertical ground (the feedback input of the amplifier). The circuit therefore ensures that the reference electrode follows the potential set at the positive input of the amplifier. The potentiostat includes additional circuitry to fulfil the following requirements: to maintain adequate voltage output to drive the required current through the cell; to provide adequate output current for the applications envisaged; to sum programming voltages from external sources to provide the waveform for various experimental techniques; and the ability to provide a voltage proportional to the cell current appropriate for driving a recording instrument. Figure 5.5(b) shows a practical circuit for doing this.

A summing amplifier A_2 provides the programming voltage E_p as the sum of component parts from an external source. Amplifier A_3 is a current follower giving a grand referenced output voltage directly proportional to the cell current.

Adaptations for Anodic Polarization Studies

Relatively minor modifications to the system were required to enable anodic polarization studies to be carried out. Since no deposition takes place on the working electrode, the 1 cm^2 planar electrodes required could be prepared by simply masking off the required area on strips of the material to be studied with P.T.F.E. tape.

The major requirement of the counter electrode is that it is of sufficient area that the processes taking place on it are not the limiting factors in the electrolytic cell, To this end a large, planar titanium electrode with a surface area of 20 cm^2 was used during these determinations.

The working electrodes were prepared as described for the titanium cathode, except in the case of the platinised titanium electrode, where such preparation would have destroyed the surface coating. This electrode was simply degreased and cleaned in the usual manner.

The reference electrode system was the same as described previously.

Procedure

Measurements

The working electrode and test electrolyte were prepared as described. The electrolyte was deoxygenated at room temperature, then heated to operating temperature where the pH was finally adjusted to the desired value.

The working electrode was fitted to the cell under nitrogen, and a 10 μm layer of iron was galvanostatically preplated at a low current density (5 mA/cm^2). The circuit was then switched to the potentiostatic mode and the point of zero current located by applying the appropriate potential across the cell via an internal reference scource from the potentiostat. A potential ramp was then applied to the electrode via the linear sweep unit at a rate of 30 mV/min. This was found to be the optimum value from preliminary work).

The cell current was recorded as a potential across a calibrated resistor, and the overpotential as a horizontal displacement with time on the chart paper. This displacement could be converted to millivolts since the sweep rate and the chart speed were known.

Presentation of Results

The polarization data was recorded using the normal electrochemical convertions with anodic and cathodic overpotentials as positive and negative quantities respectively on the y axis and current density displayed on the x axis. In most of the data the logarithm of the current density was recorded so that some expansion of the lower current densities could be obtained.

(ii) Rotating Cylinder Electrode and Divided Cell Studies

Introduction

The simple electrolytic cell utilising planar electrodes as described in the previous section exhibited a number of limitations. These are considered in detail in the Discussion section of this work. Essentially, they reduced the degree of accuracy and reproducibility of the work, and curtailed the amount of information that could be extracted from the system about the deposition processes involved.

General Arrangement

The general arrangement of the modified cell and associated equipment is shown in Plate 1. The major development to the system was the installation of a titanium rotating cylinder electrode as a cathode. This electrode rotated about a vertical axis and was located at the centre of a cylindrical graphite anode. The cell was later further modified by fitting a container constructed of an ion exchange membrane material between the cathode and anode. The basic cell is shown in Plate 2.

The auxiliary equipment is essentially as described in the last section, except that an electric motor with associated control gear and a mercury well electrical contact system have had to be incorporated to drive and supply the electrode.

Rotating Cylinder Electrode

The rotating cylinder electrode used for most of this work is shown in Plate 3 and Fig. 5.6. It consisted of interchangeable titanium cylinders of the dimensions shown, and surface areas of 1, 2 and 4 cm^2. Close fitting P.T.F.E. and caps were located on the ends of the electrode to ensure that electrodeposition took place only on the cylindrical surface of the electrode. The lower end cap was located by a nylon screw, the upper one was clamped between the top of the electrode and the end of a 6.25 mm diameter stainless steel shaft. This shaft connected the drive motor to the electrode via a precision bit and collet. The shaft entered the cell via a P.T.F.E. stirring gland fitted with a felt washer using silicone grease to form a seal. The section of the shaft inside the cell was protected from the solution by a silicone rubber sleeve. In order to minimise the effects of any eccentricity of the shaft, its length was kept to a minimum. To facilitate this, the length of the vessel used for the cell was reduced by about 3 cm.

The electrical contact to the shaft and electrode was made via a mercury well situated near to the top of the shaft. This arrangement was found to be satisfactory for the currents and rotation velocities involved.

Counter Electrodes

The counter electrode used in conjunction with the rotating cylinder electrode is shown in Fig. 5.6 and 'in situ' in Plate 2. It consisted of a piece of electrolytic grade graphite of annular cross-section, mounted in the cell so that it was concentric with the working electrode. The electrical supply to the graphite ring was via a P.T.F.E. masked titanium rod threaded directly into the graphite.

Reference Electrode System

The reference electrode system previously described, using a ceramic tipped Luggin probe for use with planar electrodes and low current densities, would not have been adequate for use in this relatively high current density application. The problem arises from the fact that in high current fields, the potential drop between the working electrode and a point in the electrolyte is relatively larger that it would be in the same situation at a lower current density. Therefore, when only low current densities(i.e. small electric fields) are involved, it is sufficiently accurate to use the relatively coarse ceramic Luggin capillary as a potential sensing probe situated approximately 1 mm from the electrode surface. With high electric fields it is essential that the tip of the probe be as close as practically possible to the electrode surface to minimise the effects of the potential drop between the electrode surface and the tip of the Luggin probe.

To meet these demands it was necessary to use a Luggin capillary as shown in Fig. 5.6. This system consisted of a 6 mm diameter 'Pyrex' tube with a fine capillary drawn at one end. The tube was fitted and adjusted so that the tip of the capillary was as close to the top of the electrode as practically possible. The electrolyte was allowed to find its natural level in the tube. A ceramic tipped Luggin was then inserted into the electrolyte contained in the tube. This Luggin capillary was connected via a ground glass top to a remote saturated calomel electrode in a 3.8 M potassium chloride reservoir.

This type of Luggin probe arrangement proved superior to the more conventional potassium chloride filled capillary Luggin. In addition to its convenience of use, it minimises the possibility of contamination of the electrolyte by the potassium chloride which forms the conducting path between the Luggin probe and the reference electrode. Leakage in this system is minimised by the ceramic tip of the Luggin probe, the use of a ground glass tap in the salt bridge and that there is no positive 'head' of solution pressure on the Luggin probe, i.e. the salt bridge reservoir should be at the same level as the tip of the probe.

Electrolytic Cell

The same type of five necked culture vessel as previously described was adapted for use with the rotating cylinder electrode. It was shortened by about 3 cm, so that the shaft length to the electrode could be kept to a minimum. As before the flask was fitted with a reflux condenser and gas jet, and a nitrogen diffuser for deaeration of the electrolyte.

The water bath no longer proved capable of heating the cell to the required temperature because of the greater heat dissipating properties of the modified electrodes. It was replaced by a magnetically stirred paraffin oil bath heated by a silica sheathed 'Red rod' heating element, thermostatically controlled by a mercury contact thermometer and associated relay system.

The arrangement of cell, oil bath, motor and ancillary equipment can be seen in Plate 1. The cell could be fixed in position in the oil bath with its centre vertically below the motor by a simple arrangement of wing nuts and clamps.

Divided Cell

Developments in the work led to the requirement for a divided electrolytic cell. A cationic ion exchange membrane (IONAC MC-3470) was selected for the function of keeping ferric ions generated at the anode away from the deposition processes taking place on the cathode.

A simple design for the cell was formulated consisting of a cylinder made from the membrane material that could be located between the cathode and the concentric anode.

Forming the flat membrane material into a cylinder proved problematical. Attempts to join the ends of the material together using various epoxy resins failed, nor did it prove possible to use silicon rubber compound to stick the ends together to form a solution proof seal. These methods were satisfactory when the membrane was dry, but when it was wetted the ion exchange resin that was impregnated onto an inert support fabric became soft and the adhesives ceased to be effective. It was known that the membrane could be welded together and that this method was sometimes used in industrial applications. Laboratory attempts to achieve a satisfactory join by various forms of heat welding were only partially successful. A strong join could be obtained, but a number of pin holes always appeared on the seams, rendering the product useless.

The problem was finally solved by clamping the ends of the membrane between two strips of polypropylene, the inner one being tapped to take 6 B.A. nylon bolts. The join was sealed by lining the interfaces with P.T.F.E. tape. The resulting cylinder was sealed at the bottom by clamping the membrane to a circular disc by a radial arrangement of 4 B.A. nylon bolts acting through a polypropylene ring. Sealing was again effected using P.T.F.E. tape. The resulting assembly is shown in Plate 4 and can be seen located in the cell in Plate 2.

R.C.E. Drive Motor and Speed Control

The drive motor used was a 'Citenco' constant torque meter, mounted horizontally above the cell (Plate 1). The motor was fitted with a worm drive gear box giving a 0-1200 rpm output and was manually speed controlled via a calibrated 10-turn wire wound potentiometer. The electrode shaft was connected to the motor via an insulated collet and a 'Jacobs' precision chuck.

The rotation velocity was initially measured and set using a calibrated stroboscope. This method proved cumbersome and a 'Farnell' digital tachometer was incorporated into the system. The tachometer was triggered by an infra-red photo-diode reflecting from a slotted aluminium disc mounted on the chuck.

Ancillary Equipment

The major items of the ancillary equipment i.e. potentiostat, linear sweep unit, potential and current measuring and recording equipment were the same as described in the section on the preliminary work. The only addition to these was the use of a 'kemitron' 1A/10A digital comtometer for measuring the current passed through the cell during current efficiency determinations. This device was connected into the counter electrode circuit and recorded directly the number of coulombs passed through the cell.

Procedure

General Preparation

Solution make-up and pH adjustment were as described in the section on Initial Work. The parameters of the electrolytes to be examined were: 3.5M ferrous chloride, pH 0.5 at a temperature of 100°C. The preparation of the rotating cylinder electrodes was similar to that described for the planar titanium electrodes, except that a small lathe was used in conjunction with the fine grade emery paper for grinding and polishing the electrodes. The test solutions were deoxygenated and heated to the operating temperature with continued nitrogen diffusion. Fresh solutions were used for each sequence of runs to avoid problems of ferrous ion concentration depletion.

Preplating and Foil Adherence Problems

A prerequisite for the measurement of the polarization characteristics of iron deposition under these conditions was the production of a reproducible, preplated layer of iron. Initial attempts were made using a cylinder with a surface area of 2 cm^2 (Height 9.09 mm, diameter 7.0 mm), to obtain a 10 µm thick iron layer at a current density of 20 mA/cm^2 in the above electrolyte at 100°C. The deposit produced would not form a consolidated adherent layer over the electrode surface, but fractured and peeled off the electrode. This was apparently due to excessive internal stress within the deposit. The first remedy tried was to preplate at lower current densities of between 5-10 mA/cm^2. This did not prove effective. It was considered that an alternative method of surface preparation might produce greater adherence between the deposit and the electrode. Three methods of chemical polishing of titanium were tested to see whether satisfactory adherence could be achieved. The chemical constituents are shown in Table 5.1. Effective as these etching solutions were in producing a well polished titanium surface, they did not provide the answer to the problem.

Another approach to reducing the effects of the internal stress in the deposit was to increase the diameter of the cylinder since the effects of the deposit stress is inversely proportional to the diameter of the electroform. The maximum possible diameter of the cylinder was limited by the size of the neck of the cell (13 mm) and the fact that the electrode and shaft had to be inserted at an angle through the neck. These considerations noted,a cylinder with a diameter of 10 mm was produced,(surface area 2 cm^2) and preplating trials made. This modification did not resolve the problem.

Minor modifications in procedure such as reducing the rotation velocity from 1200 rpm to 600 rpm and then to 200 rpm, or experimenting with different thicknesses of the preplated layer, failed to produce an adherent deposit.

It was then decided that rotating cylinder electrodes made of different materials should prove effective in surmounting the problem. Cylinders of'18/8' stainless steel, nickel and copper were made and used in the cell. They proved to be a partial answer, in that an adherent deposit could be produced on them, on which polarization determinations could be carried out. However, they gave rise to a major drawback. These metals lacked the tenacious oxide layer that was present on the titanium electrode, this meant that the iron electrodeposit adhered so well to the substrate that the only way to remove it was to machine the electrodeposit off. In addition to being tedious this was undesirable for academic reasons considered in the Discussion section of this thesis.

Further consideration of the problem indicated that if the pH of electrolyte was increased, there would be a reduction in the amount of hydrogen evolution. A reduction in hydrogen evolution should lead to a diminution of hydrogen embrittlement of the deposit. To test this hypothesis, the pH was increased from 0.5 to 1.0 (a larger increase would lead to excessive quantities of ferric ions). This modification of the electrolyte proved immediately effective and a smooth, relatively ductile and adherent deposit could be produced on a titanium cylinder. At the conclusion of a polarization determination, or for current efficiency determinations, the iron electrodeposit could easily be peeled off the electrode.

Polarization Measurements

The preparation of the electrode and the test electrolytes has been described. The procedure followed was basically similar to that described for the work with planar electrodes. A series of preliminary determinations indicated that only during the initial stages of the polarization sweep was the process mass transfer controlled. The rotational velocity of the cathode was, therefore, not critical providing it was sufficient to be well into the turbulent regime and that it did not allow bubbles of hydrogen gas to build up on the surface of the deposit. The majority of the determinations were carried out at a rotational rate of 600 rpm. The sweep rate for the potential ramp was again 30 mV/min.

Analysis of Ferrous and Ferric Ion Concentration

The electrolyte consisted of an acidic solution of approximately 3.5 M ferrous chloride containing small percentages of ferric chloride and solid ferric compounds. These could be determined separately or as combinations.

The most satisfactory method for determining the concentration of these ions is by volumetric titration against potassium dichromate. The orange dichromate salt is reduced by ferrous ions to a green chromic salt:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

from which it follows that the equivalent weight is one-sixth the molecular weight.

The ferrous ion concentration can be determined directly by titration. The concentration of ferric ion and the total iron content of the electrolyte must, however, be determined by difference, since the ferrous ion is the reactive species in the determination reaction. Ferric ions must first be reduced to ferrous, this is most conveniently facilitated by stannous chloride. Titration of the reduced electrolyte against potassium dichromate solution will indicate the total iron concentration (i.e. ferrous and ferric), and by subtracting the result of a ferrous only determination, the ferric ion concentration can be obtained.

The detailed procedure for the determination and analytical background is given by Vogel(237). For this work, 10 ml aliquots of the electrolyte were sampled. The concentration of the standard potassium dichromate was made up so that the Burette reading could be directly related to the concentration of ferrous ions in the electrolyte (i.e. 30.00 mls ≡ 3.00 M Fe(II) . The redox indicator used was sodium diphenylomine sulphate, the end point being a permanent colour change from green to purple.

Cathode Current Efficiency Determination

The current efficiency for the deposition of iron from the described electrolyte was measured under a variety of conditions. For greater accuracy of determination, a larger ($4\ cm^2$) rotating cylinder electrode was designed and constructed. The greater surface area allowed a greater mass of iron to be deposited, thus mass determinations would be more accurate.

The current efficiency runs were invariably done galvanostatically at a preset current density. The number of coulombs of electricity passed through the system was measured by a 'Kemitron' 1A/10A digital coulometer, the results obtained on this device were checked with a stop-watch and careful monitoring of the cell current.

The mass of the deposit was determined by weighing the cylinder and deposit together, then removing the deposit by peeling it from the cylinder and reweighing the cylinder. It was estimated that the determinations were carried out to an accuracy of better than ± 1.0%

Reduction of Ferric Ions by Hydrazine Dihydrochloride

The factors leading to the choice of hydrazine dihydrochloride as a possible reducing agent for ferric ions are considered in the Discussion chapter of this thesis. The relevant half reactions are also given.

Initial attempts to use aqueous hydrazine were unsuccessful due to its basic nature. This caused an immediate precipitation of iron hydroxides on additon. Additon of the hydrazine with vigorous agitation, as a dilute solution and at a range of temperatures did not overcome the precipitation problem.

To determine the effects of hydrazine dihydrochloride on the electrolyte, a stoichiometric equivalent was added to the electrolyte, and the ferrous and ferric ion concentrations analysed periodically for up to 18 hours. This was repeated for different initial concentrations of ferric ion, and further determinations were carried out to assess the effect on the rate and degree of reduction of leaving the electrolyte open to atmospheric oxidation rather than protecting it by nitrogen diffusion.

The efficacy of this reducing agent during the actual plating process was tested by carrying out plating runs in an open (undivided) cell whilst monitoring the build-up of ferric ions in the solutions. A stoichiometric equivalent of hydrazine dihydrochloride was then added while plating continued, and the ferric ion levels monitored periodically as before, by titration.

Operation with Divided Cell

No major changes in procedure were required with the ion exchange membrane modification to the reaction cell. An additional nitrogen diffuser was installed so that both the catholyte and anolyte could be deoxygenated.

The volume of the catholyte was 85 cm^3, and since the maximum weight of iron deposited during any determination was less than 0.15 g, the depletion of the iron in the solution never exceeded 1%.

Electrochemical Reduction of Electrolyte

The attempt to reduce ferric ions to ferrous by direct electrochemical reduction was made possible by the incorporation of the ion exchange membrane into the system, as this prevented ferric ions formed at the anode is kept away from the cathode.

The reduction was carried out under conditions of open and closed atmospheres i.e. with and without the effects of atmospheric oxidation.

The cathode was galvanostatically preplated to a thickness of 10 µm, and a polarization run initiated. When the 'plateau' due to the Fe^{3+}/Fe^{2+} limiting current density was observed, the potential sweep was stopped and then potentiostatically maintained at that value (550-600 mV vs S.C.E.). The decay of the cell current was then maintained over a period of up to six hours until the cathode current density appeared to reach a steady minimum. The ferric and ferrous ion concentration levels were determined at the start and end of each run, but obviously could not be sampled during the run as the volume of the catholyte would be depleted.

Complete control of the initial ferric ion concentration levels was not possible during the determinations where the electrolyte was open to atmospheric oxidation, and the initial ferric ion concentration level during these runs was obviously higher as the solution had been subject to increased oxidation.

The procedure is therefore not quantitative, but to ensure that the results observed were reasonably consistent a number of determinations were carried out, typical results of which are shown in Fig. 6.37.

Addition of Surface Active Agents (Surfactants)

The choice of surfactant is discussed in Chapter 7 of this thesis.

All of the determinations of the polarization carried out in this section of the work were conducted using the divided cell described. This was to ensure that the other variables, particularly the ferric ion concentration were kept constant.

The electrolyte was first 'prereduced' to minimise the ferric ion concentration so that possible changes observed in the polarization characteristics could not be attributed to this factor. The prereduction was carried out electrochemically under nitrogen protection as described in the previous section.

The concentrations of surfactant used were based on levels described by the manufacturers. An initial polarization run was carried out in an electrolyte containing no additive, this was used for the base comparison. Further runs were then carried out with an increasing concentration of surfactant added. The other solution parameters was as normal and are given on the appropriate figures.

VI. RESULTS

1. Conductivity Measurements

Figures 6.1-6.6 show the variation of conductivity with temperature, firstly (Fig. 6.1) for ferrous chloride only at concentrations of between 1.0-3.5 M. These can be seen to increase in an approximately linear fashion over the temperature range (20°-90°C) examined. The remaining Figs. 6.2-6.6 show the effects of additions of $CaCl_2$, $MgCl_2$, NaCl, NH_4Cl and KCl respectively. The concentrations of the additions are indicated on the figures.

Figure 6.7 shows the effect of change in ferrous chloride concentration on its conductivity at a number of temperatures between 20°C and 90°C. Figures 6.8-6.12 illustrate how the addition of increasing concentrations of conductivity salts to a base solution of 1.5 M ferrous chloride affected the solution's conductivity.

Figure 6.13 shows the results obtained when the pH of a 3.5 M ferrous chloride solution was varied between pH 0-1.2. It should be noted that this represents more than a ten-fold increase in hydrogen ion concentration.

Figure 6.14 is a summary of some of the conductivity/ temperature results. It compares the effect on the conductivity-temperature relationship of 1.5 M additions of the salts listed above.

Figure 6.15 summarises the variation of conductivity with concentration of conductivity salts at a constant temperature of 90°C.

Figure 6.16 is an Arrhenius plot of the conductivity/temperature results. This was carried out in an attempt to establish whether or not the relationship was purely exponentially related.

2. Polarization and other Work

Figures 6.17-6.20 cover some of the initial problems that arose during the early attempts to obtain polarization information from the system. Figure 6.17 shows the effects of fractures occuring in the electrodeposit during the plating process, the numbers 1-5 on the graph indicate where major fracturing occured. Figure 6.18 is an attempt to indicate the extent of 'electrochemical noise' in the system at a range of temperatures. Figure 6.19 allows a direct comparison to be made between the result from a typical rotating cylinder determination and planar electrode/nitrogen agitation (Fig. 6.18) results. Figure 6.20 shows the result of two consecutive polarization runs in the same solution under supposedly identical conditions. There is a significant increase in the magnitude of the current density at which the plateau centred at 650 mV vs S.C.E., occurs. A possible explanation of this result is discussed later.

Figure 6.21 is a summary of the initial polarization data obtained from the 3.5 M ferrous chloride electrolyte at pH 0.5 and the temperatures indicated (20°C-100°C) using the 1 cm^2 planar titanium cathode. For reasons discussed in the next chapter, the polarization curves have been limited to a current density of 10 mA/cm^2. The main features shown are the steady depolarization of the reaction with increased temperature, and increasing presence of a limiting current density at lower overpotentials.

Figures 6.22-6.25 show the results of the anodic polarization determinations carried out using planar 1 cm^2 electrodes in a 3.5 M ferrous chloride electrolyte and a mixed (20:1) ferrous chloride/ferrous sulphate electrolyte, (Total Fe = 3.5 M) at a temperature of 50°C and pH 0.5. These results are summarised in Fig. 6.26, from which a comparison of the degree of polarization and effective current densities can be made. Figure 6.27 shows the corresponding cathodic polarization data from the 20:1 $Cl:SO_4^{2-}$ electrolyte at temperatures between 60-100°C.

The polarization curves shown in Fig. 6.28 were obtained using a 2 cm^2 stainless steel rotating a cylinder cathode in a 3.5 M ferrous chloride electrolyte at pH 0.5 and a temperature of 100°C, after first preplating with a layer of iron. These were produced when difficulties were being experienced in obtaining an adherent deposit on a titanium rotating cylinder electrode. Similar results were achieved using nickel and copper cylinders.

Figure 6.29 shows the polarization curves obtained once the adhesion problem had been solved by changing the pH of the test electrolyte from 0.5 to 1.0. All the remaining work was carried out at this latter pH. As with previous successive determinations in the same sample of electrolyte, an increase in the limiting current density plateau can be seen.

Figure 6.30 relates the decrease in the cathode current efficiency with the number of coulombs of electricity passed through the electrolyte. The efficiency falls off quite rapidly, but appears to be approaching a minimum at about 90%. This result can be compared with the data summarised in Fig. 6.31, where the increase in the concentration of ferric ions has been determined as a fraction of the amount of electricity passed through the electrolyte. The ferric ion concentration builds up from its initial concentration of 0.04 M to what appears to be an equilibrium value of approximately 0.10-0.11 M. At this concentration it would appear to be reduced at the cathode at the same rate as it is being produced at the anode.

The polarization curves shown in Fig. 6.32 were obtained using the usual electrolyte, but on this occasion treating it with hydrazine hydrate. Some iron hydroxide precipitation occured but this was removed by filtration, the resulting electrolyte was a clear green indicating a substantial reduction in ferric ion concentration. The polarization curves shown support this, in that the current densities on the Fe^{3+}/Fe^{2+} plateau are significantly lower than those obtained using the normal electrolyte. The second and third curves in this figure were obtained on subsequent runs, the latter being made after an interval of approximately 18 hours where the additional effect of atmospheric oxidation can be observed.

Figures 6.33 and 6.34 show the results obtained when (Fig. 6.33) hydrazine hydrochloride was used to reduce a solution of ferrous chloride containing ferric ions at a concentration of 0.10 M. The concentration of ferric ions was monitored at intervals and the resultant concentration decay plotted. This was done in solutions pretreated by an inert (N_2) atmosphere and in solutions open to atmospheric oxidation. Figure 6.34 shows the dynamic equivalent to the previous results. Here a stoichiometric equivalent of hydrazine dihydrochloride has been added to the on going plating process, where the build-up of ferric ions in the undivided cell has been monitored. A decrease in the ferric ion concentration is observed after the addition, but to a much smaller extent than the static system, since in this case the production of ferric ions at the anode must be countered.

Figure 6.35 illustrates the effect of the insertion of the ion exchange membrane between the cathode and anode on the power requirements of the laboratory rotating cylinder electrode cell. It shows that, as would be expected, there is a penalty in terms of greater cell voltage requirements for a given current density.

Figure 6.36 shows an example of a polarization curve obtained using the divided cell system. There is still a small inflexion probably due to the remaining presence of a small concentration of ferric ions. The important aspect of this determiantion was that subsequent determinations in the same electrolyte were essentially identical to the curve shown in the figure. This is a strong indication that the membrane is acting as intended in preventing build-up of ferric ions in the catholyte.

Figure 6.37 shows a typical result obtained from the divided cell system when the ferric ions were reduced electrochemically under potentiostatic control. The upper line was obtained using a solution left open to the effects of atmospheric oxidation, where the initial concentration of ferric ions will be high. The lower curve results from a solution that had been deoxygenated and kept under a nitrogen blanket. Both curves show an almost exponential decrease to a minimum at approximately five hours. The residual current at this time is most probably due to small amounts of ferric ions being produced by oxidation due to traces of impurities and trace oxygen in the nitrogen supply.

Figures 6.38 - 6.40 show the polarization curves obtained when small traces of cationic, anionic and non ionic surfactants were added to the basic electrolyte. There has not been a significant change in polarization characteristics, the minor variation that can be seen in the results fall within the area of experimental limitations.

VII. DISCUSSION

1. Conductivity Survey

In commercial electroplating the amount of electrical power consumed is of major importance, and every effort is necessary to reduce it to a minimum.

Electrical power is purchased by the watt (i.e. in units of volts x amps). Simple faradaic considerations show that the quantity of product obtained from the electrodeposition process is directly proportional to the number of coulombs and thus current passed through the system. In the case of the hot ferrous chloride electrolyte, the plating efficiency has been shown to be nearly 100%. Hence there is only the possibility for marginal improvement in the economy of the process from study of this aspect of the electrical equation.

It is immediately apparent that if significant savings are to be made then they must come from a reduction in the voltage requirements of the system. To this end, the following areas must be examined. The electrochemical plant must be designed and engineered to reduce voltage drops to an absolute minimum. This area is somewhat outside the scope of this project; however, the more important points include suitable choice of conducting materials and connections to the electrochemical reactor, the use of good electrical brushes to the rotating cylinder and the ensurance of good conducting pathways inside the cylinder. Within the reactor, the inter-electrode spacing is critical. This is a compromise between allowing a large enough gap for the flow of sufficient electrolyte to avoid significant solution depletion, and to minimise the effect of localised unevenness in the gap as the anode wears; and small enough to keep the ohmic drop and hence resistive losses across the cell to a minimum.

A number of secondary reactions in the process may also lead to increased power consumption. The first of these is hydrogen evolution, this should not be a serious problem in a well controlled ferrous chloride bath provided that the pH of the solution is kept above 0.5, as deposition will proceed at almost 100% efficiency. The presence of iron (III) will have a deleterious effect on power consumption. Firstly, from simple electrochemical considerations in that an iron (III) cation formed at the anode or already present in the solution will require an additional electron to reduce it to iron at the cathode. Secondly, there is the purely physical effect of coating of the anode by hydrated ferric oxide deposits.

The review of the electrodeposition of iron from various electrolytes indicated the evolution of factors leading to the choice of hot ferrous chloride as the optimum electrolyte for electrolytic iron foil production. Given this electrolyte, it was apparent that a study of the conductivity characteristics of the electrolyte and the effects of the addition of conductivity salts could indicate whether improvement in solution conductivity was possible, leading to reduced power consumption.

The major criteria in the choice of possible conductivity salts are equivalent conductivity, solubility, stability, cost and absence of adverse effect on the deposit. The latter factor excludes serious consideration of many compounds whose ions would lead either directly or indirectly to deleterious effects in the deposit. From these considerations five compounds were short listed for study (see Table 7.1).

It is important to note that the salts were all added to a background concentration of 1.5M ferrous chloride. This amount was chosen as a standard background so that a reasonable range of concentration of conductivity salt could be studied. Significantly greater a concentration of ferrous chloride would have meant that a smaller concentration of conductivity salt could be added as the common ion effect soon increases the solubility product to saturation.

The general trend of conductivity with temperature as shown in Figs. 6.1 to 6.6 was similar for all the solutions studied. The essentially linear increase in conductivity with temperature is in agreement with the trends shown for concentrated chromic acid solutions by Groeneboer(245).

Intuitively, one might expect the variation of conductivity with temperature to be a thermally activated process and hence obey the Arrhenius equation, which has the following form:

$$\text{Conductivity} = A \exp -\left(\frac{\Delta G^{o}}{RT}\right) \quad \ldots\ldots \quad \text{Equation 7.1}$$

where A is a constant, ΔG^{o} is the standard free energy of activation, R and T, the gas constant and absolute temperature respectively. This being the case, a plot of log conductivity against the inverse of absolute temperature should result in a straight line relationship, having a slope of - $(\frac{\Delta G^{o}}{R})$.

However, as can be seen from Fig. 6.16, none of the solutions showed this type of behaviour. All of the plots exhibit some degree of curvature, thus indicating that the process is not purely thermally activated.

The relationship between conductivity and temperature is complex. There are many factors that determine the conductivity of a solution including viscosity, diffusion processes and ionic processes. The temperature dependence of conductivity upon each of these physical characteristics is different and they do not combine to give a purely exponentially related relationship. For example, in the equation relating the diffusion coefficent and temperature;

$$D = \tfrac{1}{2}\ell^{2} \frac{kT}{h} e^{-\Delta G^{o}/RT} \quad \ldots\ldots \quad \text{Equation 7.2}$$

where: ℓ is the mean jump distance of a molecule

h is the Planck constant

k is the Boltzman constant

G^{o} is the standard free energy

R is the Gas constant.

It can be seen that not only is there an exponential relationship between the two quantities but also a direct linear relationship.

The variation of the conductivity with concentration summarised in Fig. 6.15 shows no predictable trend as would have been expected had a survey of very dilute solutions been carried out. In general, the results indicate that the addition of conductivity salts in the concentrations shown does lead to an increase in solution conductivity when compared with the basic 1.5M ferrous chloride solution. In the cases of magnesium chloride and calcium chloride the increase is marginal (between 0.015 and 0.05 Ω^{-1} cm^{-1}). The addition of up to 2.0 moles of sodium chloride to a 1.5 M ferrous chloride solution will lead to an increase in conductivity of approximately 0.05 Ω^{-1} cm^{-1}. More interesting are the results for potassium chloride and ammonium chloride. As can be seen from Fig. 6.15 an addition of less than 0.5 moles of KCl to 1.5 M $FeCl_2$ will give an increase in conductivity of more than 0.12 Ω^{-1} cm^{-1} when compared with the basic 1.5 M solution. An even more pronounced effect is produced by the addition of between 2 and 3 moles of ammonium chloride to the base solution.

However, to some extent these results are misleading. The problem of solubility mentioned before is an important factor. In order to maximise the current at which iron can be deposited, it is necessary to maximise the concentration of iron in the electrolyte. To do this a ferrous chloride solution is chosen so that it is as near to being saturated as possible. The only limitation being the practical consideration that the salt must not crystallise out when the solution is allowed to cool. Thus, although the conductivity of a rather less concentrated iron chloride solution can be increased by the addition of the above salts, this 'remedy' is not possible when using an almost saturated iron chloride solution.

The relatively unpredictable nature of the relationship between conductivity and concentration in these solutions is not entirely unexpected. The reason for this is that the values of ionic mobility and conductance from which the theory has been evolved and proven apply only to electrolyte solutions of very low ionic concentration, and even the development of the subject over the years has only managed to account for the behaviour of a few simple solutions of concentrations up to only about 0.1 M.

The behaviour of the hot and nearly saturated solution of ferrous chloride bears little resemblance to the solutions used in the development of classic solution theory. Values for ionic conductivities are usually given only for solutions of infinite dilution i.e. the ideal case where the ions can be considered to be acting independently and ionic salts are fully dissociated. This is clearly not the case for the ferrous chloride electrolyte which is highly concentrated giving rise to large ionic interactions. The ionic interaction occurs in a number of ways. /Firstly, there is an electrophoretic effect arising when an ion moves through a viscous medium tending to drag along with it the solution in its vicinity. Neighbouring ions therefore have to move not in a stationary medium but with or against the stream. This effect is highly concentration dependent, falling to zero at infinite dilution. The second major effect in less dilute solutions is the relaxation effect. This effect can be illustrated by considering a single ion surrounded more by an oppositely charged ion atmosphere. The application of an electric field results initially in the movement of the central ion from the centre of the sphere. The distorted ion atmosphere tends to oppose the applied field and this decreases the movement of the ion in the field. The ionic atmosphere drag depends on the fact that the atmosphere does not instantaneously adjust itself to the new positions of the central ion. The decrease in movement increases at higher concentrations since the ion atmosphere becomes more important.

A more specific attraction between oppositely charged ions must also be recognised at the high concentrations being considered. This is the formation of ion pairs or ion triplets. In the case of a symmetrical electrolyte such ion pairs will have no net charge, though they will have a dipole moment. They will therefore make no contribution to the electrical conductivity, while their thermodynamic effects will be those of removing some of the ions from solution and replacing them with dipolar 'molecules'. With the unsymmetric salts, the situation will be more complicated, since the simplest and most probable type of association, that involving two particles will result in the appearance of a new ionic species of a charge type not previously present; this will contribute to the condcutivity, though less than would its constituent ions in a free state. Also in this case further association to form neutral particles can be expected.

Considered together, these effects cause large deviations from the ideal behaviour of nearly infinitely dilute solutions, and show why it is difficult to make quantitative or qualitative predictions in an attempt to rationalise the behaviour of the ferrous chloride electrolytes. Thus, the information obtained from the conductivity measurements discussed here must be considered and applied empirically and relative to the particular application of electroforming in this type of plant.

Examination of values of ionic conductance shows that the ionic conductances of the hydroxonium ion is about five times the average for other ions. It would thus be anticipated that the pH of the plating solution would be an important factor in the solution conductivity.

Figure 6.13 shows the results obtained from the determination of the conductivity of 3.5 M $FeCl_2$ at pH's of between 0.1 and 1.1. It can immediately be seen that over the stated range of pH the conductivity of the solution does not appear to vary within experimental limits of detection.

It is at first apparently anomalous that a tenfold change in the concentration of the highly mobile hydroxonium ion should have a negligible effect on the conductivity of the electrolyte.

In order to suggest an answer to this apparent anomaly one must seek a quantitative measure of the extent to which each ionic species carries the current. This quantitative measure is the transport number (t_i) defined as the fraction of the total current carried by the particular ionic species:

i.e. $$t_i = \frac{i_i}{i_T} = \frac{i_i}{\Sigma i} \quad \ldots\ldots \qquad \text{Equation 7.3}$$

This definition requires that the sum of the transport numbers of all the ionic species be unity for:

$$\Sigma t_i = \Sigma \frac{i_i}{\Sigma i_i} = 1 \quad \ldots\ldots \quad \text{Equation 7.4}$$

The problem in question can most easily be illustrated by consideration of a mixture of the univalent electrolytes HCl and KCl. The mobilities (U) of the H^+ and Cl^- ions in 0.1 M HCl at 25°C are 33.71×10^{-4} and 6.84×10^{-4} cm sec^{-1} V cm^{-1}, respectively. These values can be substituted in the relationships:

$$t_{H+} = \frac{U_{H+}}{U_{H+}+U_{Cl^-}} \quad \ldots\ldots\ldots \quad \text{Equation 7.5}$$

and

$$t_{Cl} = \frac{U_{Cl^-}}{U_{H+}+U_{Cl^-}} \quad \ldots\ldots\ldots \quad \text{Equation 7.6}$$

(The derivation of the above is given by Bockris and Reddy(238).

Substitution shows that the transport numbers of the H^+ and Cl^- ions are 0.83 and 0.17 respectively. Thus the positive ions carry the major portion of the current.

Now, in a solution where there is a major excess, of say KCl (as there would be in the modified iron plating solutions) where the K^+ concentration is 1 M and the H^+ concentration 10^{-3}M, the transport numbers in the mixture of electrolytes will be:

$$\frac{t_{K+}}{t_{H+}} = \frac{C_{K+}\, U_{K+} \,/\, \Sigma C_i U_i}{C_{H^+}\, U_{H+} \,/\, \Sigma C_i U_i} \quad \ldots\ldots\ldots \quad \text{Equation 7.7}$$

$$= \frac{C_{K+}}{C_{H^+}} \cdot \frac{U_{K^+}}{U_{H^+}} \quad \ldots\ldots\ldots \quad \text{Equation 7.8}$$

Hence, $t_{K+} = 200$

which means that although the H^+ ion is about five times more mobile than the K^+ ion it carries 200 times less current. Thus the variation of the H^+ concentration in an excess of other ions i.e. Fe^{2+}, K^+ etc., has a negligible effect on the current carrying capacity of the solution i.e. the conductivity is little affected. In fact, the transport number of the H^+ ions in such circumstances is virtually zero, as shown by the following approximate calculation:

$$t_{H+} = \frac{C_{H+} U_{H+}}{C_{H+}U_{H} + C_{K+}U_{K+} + C_{Cl-}U_{Cl}} \quad \ldots\ldots \quad \text{Equation 7.9}$$

$$\doteq \frac{10^{-6}U_{H}}{10^{-6}U_{H+} + 10^{-3}U_{K+} + 10^{-3}U_{Cl^-}} \quad \ldots\ldots \quad \text{Equation 7.10}$$

Therefore $t_{H+} = 10^{-3}$

Thus the conduction current carried by the ion depends very much on the concentration in which the other ions are present.

From the results and consideration of solubility factors, it is reasonably conclusive that major improvements in the conductivity of the hot and almost saturated ferrous chloride plating solution cannot be made. The case for additions of 'conductivity salts' to a less concentrated (e.g. 1.5 M) ferrous chloride solution is stronger. As Fig. 6.15 indicates, significant increases in electrolyte conductivity can be obtained from addition of KCl, NaCl and particularly NH_4Cl. If this approach to improved solution performance is to be seriously contemplated, then the bulk costs of the chemicals must be considered in comparison with the quantity of the addition necessary since conductivity is a colligative property of the salt. The approximate wholesale bulk cost (1981 prices) of the salts used are shown in Table 7.2. From this it can be seen that the most 'effective' conductivity salts are available at relatively competitive bulk prices.

The argument for the use of a less concentrated ferrous chloride electrolyte combined with the addition of a conductivity salt merits serious consideration. In a high production electroforming process one seeks a balance between the conductivity of the solution, which must be maximised to reduce power consumption, and the concentration of the solution which one seeks to maximise so that a higher rate of deposition may be obtained without the reaction running into concentration polarization limitations. These requirements are contradictory, because at the levels of concentration being considered, the conductivity of the electrolyte decreases with increasing concentration for the reasons discussed. Therefore, any attempt to increase concentration so that deposition rate may be maximised is done at the price of reduced conductivity. However, for the system under consideration, study of the polarization data shown in this thesis shows that at no time has the main deposition reaction passed into concentration polarization. This means that some reduction in ferrous chloride concentration may well be possible without significant adverse effect to the polarization characteristics of the system. With reduced ferrous chloride concentration comes increased conductivity due to reduced ionic interaction. Furthermore, it then becomes possible to make conductivity salt additions which will lead to further significant increases in solution conductivity.

It is important that these factors should not be considered in isolation. Although some reduction in concentration should be possible without affecting the limiting deposition current, it should be noted that the deposition overpotential will be increased leading to greater voltage and hence power requirements. Further work would need to be carried out to determine the extent to which the concentration of the electrolyte could be reduced without detrimental effect to either the process or the product.

The dilemma may be illustrated by an example which could well be employed as a plant trial. The major portion of the potential difference between two electrodes in a solution occurs across the two electrode solution interfaces which immediately means that any saving due to increase of the solution conductivity will only lead to reduction in the minor portion of the potential difference across the cell. A reasonable approximation of the potential difference across the interelectrode gap in a plant electroforming at about $4000 A/m^2$ is 6.0V. From the summary of conductivity results one can see that a combination of reduced ferrous chloride concentration (to about 2M), and addition of either ammonium, potassium or sodium chloride will give an increase in conductivity of approximately $0.1\ \Omega^{-1}\ cm^{-1}$ i.e. $\sim 30\%$. If it is assumed that the contribution of the solution portion of the potential drop to the overall cell voltage is about 20% of the total, the simple calculation shows that a saving of 0.36V will result. Although this saving may appear relatively small

(6%) its significance becomes more obvious when considered in terms of production plant operation, where one may be operating a 40 kA cell at 6V i.e. a consumption of 240 kW, the saving then is 14.4 kW, a substantial amount of power! It is possible that the proportion of potential difference attributable to solution conductivity is in practice rather greater, say 30% rather than the 20%, in which case the savings are of course proportionally greater.

2. Polarization and Other Work

The principal aims of this section of the work were to attempt to establish the basic polarization characteristics of the iron electroforming system. This was not as straightforward as was initially anticipated and involved a long series of developments and modifications of the experimental system. Having surmounted these problems and established the polarization data, other aspects of the system could be studied and possible methods of optimisation explored.

Solution Equilibrium

The acquisition of reproducible electrochemical data from the ferrous chloride electrolyte, especially at elevated temperatures, provided a continuing challenge throughout the duration of this project. It is well-known that the divalent ferrous ion in aqueous ferrous chloride is prone to atmospheric oxidation, the mechanism of which has been suggested by Goto, Tamura and Nagayama(239). As early as 1906, Just(240) had shown that the rate of oxidation of ferrous iron by dissolved oxygen can be expressed by:

$$-\frac{d\,[\mathrm{Fe(ii)}]}{dt} = k_o\,[\mathrm{Fe(ii)}]\,[O_2]\,[OH^-]^2 \qquad \text{Equation 7.11}$$

This relationship is important as it indicates not only the significance of minimising the dissolved oxygen in the system, but also the importance of the pH of the solution and that there will be change in the solution pH as ferrous ions are oxidised. An additional complication to the system is that the ferric ion formed as an oxidation product is hydrolysed to a much greater extent than ferrous chloride, and the products of this hydrolysis tend to be precipitated:

$Fe^{3+} + H_2O \rightleftharpoons (FeOH)^{++} \downarrow + H^+$ .... Equation 7.12

Solutions containing appreciable amounts of ferric ion will be brown and cloudy as a consequence of this hydrolysis. It has been suggested (241) that these hydrolysis products can be incorporated into the foil deposit giving rise to pin holing. On the laboratory scale the presence of ferric ions in the solution proved to have a substantial effect on the deposition of iron.

The major quantity of ferric ions in the electroforming system under consideration is, however, produced by anodic oxidation of ferrous ions. Examination of the standard oxidation potentials of the reactions possible at the anode shows that the reaction occurred will be oxidation of ferrous ion to ferric ion:

$H_2O \rightleftharpoons \frac{1}{2}O_2 + 2H^+ + 2e^-$ E^o_{298} +1.23V Equation 7.13

$Cl^- \rightleftharpoons \frac{1}{2}Cl_2 + e^-$ $E^o_{298} = +1.36V$ Equation 7.14

$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$ $E^o_{298} = +0.77V$ Equation 7.15

Considering the iron reactions at the anode and cathode together, the overall reaction of iron deposition is:

$3Fe^{2+} \rightarrow 2Fe^{3+} + Fe$ ..... Equation 7.16

Hence for every mole of iron deposited two moles of ferrous ion are oxidised to the ferric state and can undergo hydrolysis.

One of the basic elements in the study of the effects of a number of variables on a system is that one should be able to keep all but one of the possible variables constant while the effects of that one variable is explored. With the above comments in mind, it can be realised that for this system fulfilment of this axiom is by no means straightforward. There is the initial difficulty of exactly defining the working solution, since even though the masses and volumes of make-up materials are known, oxidation will slowly change this composition. There will be an increase in the ferric ion concentration a corresponding decrease in ferrous ion concentration and a change in the pH of the solution. The situation is further complicated when electrodeposition takes place, for in addition to the possible effects of atmospheric oxidation, ferric ions will also be produced in quantity by anodic oxidation at the insoluble anode. At higher overpotentials, further localised changes in pH may be produced by hydrogen evolution at the cathode. Finally,the ferrous ion level will be additionally diminished during electrodeposition. Thus the study of the ferrous chloride electrolyte system demands, firstly, every precaution to minimise adverse effects and, secondly, an acceptance that there will necessarily be some unavoidable limitations on the accuracy and in the interpretation of the data obtained.

Cathodic Reactions

The initial polarization work was an attempt to establish the basic cathodic polarization characteristics of iron deposition from a 3.5 M ferrous chloride electrolyte, at a range of temperatures from room temperature up to just below the boiling point of the solution. A number of problems manifested themselves during this initial work. One of the major early difficulties is illustrated on the polarization curve shown in Fig. 6.17. At the points indicated (1-5) there has been a sudden increase in the 'apparent' current density. This was associated with the appearance of fractures in the electrodeposit. When these occurred their effect was to increase the cathodic surface area, and since the polarization was carried out under potentiostatic control, there is a sudden increase in the current flowing through the cell. This problem was particularly noticeable when attempting to obtain polarization data at lower temperatures when fracturing occurred at very low current densities, often less than 10 mA/cm^2. As the temperature was increased, higher current densities could be attained before fracturing occurred. A possible explanation of this occurrence comes from consideration of the properties of iron electrodeposits from the ferrous chloride solution. At temperatures of below approximately 85-90°C the deposit is very stressed and brittle, an effect which becomes more pronounced at lower temperatures. Thus, as the thickness of the deposit increases so do the internal stresses until the point where the deposit fractures and the stress is relieved. This result is obviously undesirable as the effective area of the cathode surface has increased by an unknown factor so that an accurate statement of the cathodic current density is no longer possible. The value obtained and shown on the current density axis is, in effect, only an apparent current density, and since the surface area has increased, the current flowing will increase and thus, the value obtained for current density is somewhat in excess of the real value.

Another undesirable feature that arose during these early polarization measurements was the presence of edge effects. Although this is not readily apparent from the polarization curve, it was immediately obvious on visual examination of the deposit on the planar electrode. The effect is well-known, and arises from increased concentrations of current density at the edges of the electrode due to the slight and unavoidable curvature of the electrode at the electrode resin interface. This anomaly does not produce as great an inaccuracy as does the fracturing of the electrodeposit. It does, however, produce a significant error in the current density values, an error which increases with increasing current density, as the deposition at the edges of the electrode becomes more nodular.

In order to avoid fracturing, and to minimise nodular growth at the edges of the deposit, it was necessary to limit the extent of polarization of the electrode so that the current density did not exceed 10 mA/cm^2 for temperatures below approximately 60^oC.

The use of nitrogen to provide solution agitation, in addition to its oxygen displacement role, was not wholly satisfactory. An attempt has been made to illustrate the problem in Fig. 6.18, where examples are shown of the recordings of cell current versus electrode potential at different temperatures. There is clearly a substantial increase in the noise level of the signal as the temperature of the electrolyte is increased. While at temperatures lower than about 80°C the noise does not seriously interfere with the interpolation of the data, at higher temperatures the noise levels are such that the general trend of the polarization curve becomes difficult to interpret with a reasonable degree of accuracy.

It was initially considered that the noise was due to bubbles of nitrogen interfering with the current path between the electrodes, and also interfering with the Luggin capillary. Modifications to the nitrogen flow though the cell afforded no significant reduction in noise levels during the high temperature runs, although at lower temperatures some of the coarser irregularities could be minimised, indicating that they had been caused by the method of agitation. From further consideration of the problem, it became apparent that the cause lay in the increasing convection currents in the solution as the temperature was raised. These currents, caused by the increased thermal activity of the system combined with its reduced viscosity, appear to affect seriously the Fe^{3+}/Fe^{2+} reduction reaction. This reaction will be discussed in detail later, As is apparent in Fig. 6.18, noise most seriously affects the area of the polarization curves that show a limiting current i.e. the reaction is exhibiting concentration polarization, indicating that some degree of uneven agitation is occurring, which, since it has been established, was not due to nitrogen agitation would appear to leave only convective currents as the possible source of this problem.

Since the reaction to be studied in detail, was to be conducted at a temperature of 100°C, it was obviously undesirable that this level of noise should be present, What was needed was some form of powerful and reproducible agitation. The answer to this problem was later provided by using a rotating cylinder electrode as the cathode. This permitted strong agitation at a known and reproducible level and, as is illustrated in Fig. 6.19, the level of noise has been greatly reduced. This reduction in noise arises from the fact that the rotating cylinder electrode produces strong turbulent flow around it which overcomes the natural convection currents in the hot electrolyte.

Further factors affecting the reproducibility and accuracy of the polarization data are indicated in Fig. 6.20. The two polarization curves shown are from successive runs in the same electrolyte, with all of the controllable physical parameters held constant. The result should have been two identical curves. This is clearly not the case, as a noticeable difference in the polarization characteristics can be observed in the potential range 560-760 mV (vs S.C.E.) The curve obtained from the second run exhibits a point of inflexion that occurs at approximately twice the current density of that of the first curve. With successive runs the plateau or inflexion occurred at progressively higher current densities. The reason for this limiting current was initially not understood, but was later established, by chemical analysis, to be a characteristic of the cathodic reduction of ferric ions which are present in small amounts ($\sim$ 3%) in the electrolyte. The fact that the limiting current density for this reaction increased on successive runs is best explained by consideration of the anodic reaction i.e. Equations 7.15 and 7.16, where it has been indicated that the predominant reaction will be the oxidation of ferrous ions to ferric ions, and that two moles of ferric ions will be produced for each mole of metallic iron deposited, thus its concentration and the limiting current density of its reduction will increase during deposition.

Another problem observed at this stage was the difficulty of obtaining reproducible rest potentials for the iron coated electrode in the electrolyte. These potentials tended to vary by up to 15 mV under conditions that were as identical as practically possible. For example, the difference in the rest potential between the two successive runs shown in Fig. 6.20 was 12 mV. It should be noted that the actual zero current potentials are not shown in the figure as the logarithmic current density scale starts at 0.1 mA/cm^2).

This degree of change cannot be explained by purely Nernstian consideration of the change in ferrous and ferric ion concentration, as this would only account for a fraction of the change in potential observed. Variation in the degree of solution agitation was shown to affect the rest potential. Thus it would appear that the differences in the values, obtained during supposedly steady agitation by a constant flow of nitrogen gas through the solution, occurred due to localised variation of the agitation over the surface of the electrode. This possibility was later confirmed during experimentation using the rotating cylinder electrode where the rest potential was observed to vary with change in the rotation velocity of the electrode.

Despite the limitations of the planar electrode and agitation by nitrogen diffusion, it was possible to obtain some useful data on the cathodic polarization characteristics of iron deposition from a concentrated iron chloride electrolyte, provided that the current density was not allowed to exceed 10 mA/cm^2, and that each run was started with a fresh solution so that the quantity of ferric ions present would be approximately the same in each case.

The results obtained from the low current density cathodic polarization runs are shown in Fig. 6.21. It can be seen that there is a significant depolarization of the reaction as the temperature is raised towards the boiling point of the electrolyte. Nernstian considerations obviously account for some of the changes in the equilibrium value of the reaction potential, i.e. as the temperature is increased there will be a change in E given by the Nernst Equation:

$$E = E_o - \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} \quad \ldots\ldots\ldots \quad \text{Equation 7.17}$$

where: E_o is the standard Potential of the system.

E is the potential under the conditions of the reaction.

R is the Gas Constant.

T is the absolute temperature.

n is the number of electrons involved in the process

F is the Faraday Constant.

For the electrolyte system under study it would be difficult to predict the exact magnitude of the change in potential with temperature, as there are many species present and a number of reactions contributing to the overall potential of the system. The major contributing reactions and their respective values of dE/dT are given below:

Reduction Couple	dE/dT mV K^{-1}		
$Fe^{2+}/Fe(s)$	+0.052	....	Equation 7.18
$2H^{+}/H_2(g)$	+0.000	....	Equation 7.19
Fe^{3+}/Fe^{2+}	+1.188	....	Equation 7.20

The hydrogen reduction reaction will obviously not contribute to a change E and is mentioned only for completeness. Since the amount of ferric ion present is also a function of the temperature of the electrolyte, attempts to estimate the overall value of dE/dT are further complicated.

For reasons discussed later in this text, no attempt has been made to derive mechanistic or kinetic data from these polarization curves. The main feature that the curves in Fig. 6.21 illustrate is the increasingly prominent plateau that becomes apparent at elevated temperatures. As explained earlier this feature is probably due to the pressure of increasing amounts of ferric ions in the solution as the temperature is increased. In addition to reducing the degree of reproducibility of the curves, the presence of varying amounts of ferric ion also tend to mask the true Fe(II)/Fe reduction characteristics, hence the problems of elucidation of mechanistic behaviour.

Industrially, the steady depolarization of the reaction with increasing temperature is important. The indication is that there are savings in the demand for electric power to be made if the basic overvoltage requirement of the system can be reduced. This consideration must be balanced by consideration of the increased heating requirements of the system at elevated temperatures.

Anodic Reactions

The anodic polarization characteristics of a number of materials were determined in this iron electroforming electrolyte in an attempt to establish which would make the most favourable anode material. The results are shown in Figs. 6.22-6.25 and summarised in Fig. 6.26.

Considering the anodic polarization curves for titanium first, it is immediately obvious from the resulting curve that this material would be very unsatisfactory from an electrochemical point of view, since at potentials of more than approximately 1400 mV (vs S.C.E.) a stable, passive oxide film is formed, and remains stable for some 1000 mV until the film is apparently broken down by the onset of oxygen evolution at approximately 2200-2400 mV (vs S.C.E.). The formation of the passive layer severely restricts the current which can pass at the anode, in this case to less than 10 mA/cm^2, before passivation occurs. It would be possible to further polarize the electrode so that it operates in the region of oxygen evolution but to do this a significant penalty, in terms of extra voltage, and hence power consumption, must be made. It is also worth noting that as the anode is to be used in an electroforming system, it would not be possible to overcome the current density limitation simply by increasing the working area of the anode since there are obvious geometric limitations to its size.

Another reason for examining the anodic polarization behaviour of titanium arose from problems in plant use where the foil was sticking to the drum surface. It was thought that this may be due to hydride formation at depassivated points on the surface and that these could be partially eliminated by having sulphate ions (a mildly passivating ion) in the solution. The result of a 20 : 1 ratio of Cl^- : SO_4^{2-} ions in the solution is also shown in Fig. 6.22. It shows clearly that there is little to be gained by this modification to the solution as the region of passivation (i.e. between 1400-2400 mV) has not been changed to any significant degree. Attempts were made to determine the effect of a larger ratio of SO_4^{2-} ions but these were not successful as ferrous sulphate is not as soluble as ferrous chloride making it impossible to obtain a 3.5 M solution of iron salts with a larger ratio of SO_4^{2-} present.

Similar determinations were made using stainless steel, the results of which are shown in Fig. 6.23. These indicate that stainless steel has much more desirable polarization characteristics than titanium when considered as a potential anode material. The curve rises steeply indicating good current flow at low overpotentials. There is some evidence of passivation of the electrode surface at potentials greater than 300 mV (vs S.C.E.), this passivation also occurs in the mixed chloride-sulphate ion electrolyte. The major disadvantage of the material is that it is unable to withstand long term chemical attack by the electrolyte and slowly etches in the solution. This is obviously undesirable as the working anode will be immersed in the electrolyte for long periods and will, of course, be anodically polarized during the plating operation and must therefore be essentially inert to the rigours of this very aggressive environment.

Very similar considerations apply to the use of platinised titanium as an anode. Its polarization characteristics, shown in Fig. 6.24 are quite favourable, showing a rapid rise to a limiting value of current density prior to the commencement of oxygen evolution. However, research at B.S.C. Swansea has shown that the platinised layer does not withstand prolonged operation in this electrolyte. This may possibly be due to inadequacies in its manufacture, causing defects in the platinum layer which allows the electrolyte to attack the titanium layer causing further separation of the platinum coating.

Graphite was the other anode material subjected to polarization studies, the results are shown in Fig. 6.25. Its polarization characteristics are very similar to those of platinised titanium showing a rapid rise in current density with low polarization, a limiting current density approximately 90 mA/cm^2 lower than that of platinised titanium, followed by a further rise in current density due to the commencement of oxygen evolution.

The graphite anode has in fact been long used in iron electroforming for many reasons in addition to its reasonable polarization characteristics. It is readily available, can be easily machined, exhibits good internal conductance and can resist chemical and electrochemical attack in this application. It is prone to mechanical erosion by the flowing electrolyte in industrial environments, this being perhaps its major disadvantage, as wear leads in time to unevenness in the anode-cathode spacing causing some degree of non-uniformity in the foil thickness. However, until the appearance and increased reliability of the new generation of dimensionally stable anodes, graphite has been the only realistic possibility for use as an anode material and it seems likely that this will continue into the foreseeable future.

While considering the possibility of using an electrolyte consisting of a 20 : 1 mixture of Cl^- : SO_4^{2-} ions, it was thought useful to determine the effect of this electrolyte on the cathodic polarization of iron. This was carried out at temperatures of 60°C, 80°C, and 100°C, and the results are shown in Fig. 6.27. Comparison of these results with those obtained at similar temperatures in a ferrous chloride electrolyte of the same concentration (Fig. 6.21) shows that curves are essentially identical within the limitations of obtainable accuracy. The increase in the limiting current density plateau present on all three curves is a result of the increased ferric ion concentration present in the solution at the elevated temperatures, due to the increased oxidation occurring during the polarization run and the preceeding preparations. Overall, it would appear that the change from the ferrous chloride to a 20 : 1 chloride:sulphate mixture has no discernable effect on the cathodic polarization characteristics.

Modified Plating Cell

The cathodic polarization data discussed so far have been limited to relatively low current densities (10-30 mA/cm^2) because of the practical limitations of the experimental arrangements described. As these limitations become apparent during the work it becomes clear that to obtain useful data at higher current densities, and at current densities of the normal industrial operating levels (i.e. $\sim$ 400-500 mA/cm^2), major modifications to the laboratory set up would be required.

The problem of the deposit fracturing is much reduced once the temperature of the electrolyte is above 80-90°C, as the deposit then becomes fairly ductile and relatively free of stress. However, the following problems remain:

1. edge effects, i.e. the build-up of deposit around the edges of the planar electrode;
2. noise probably produced by unsuppressed natural convection currents in the hot electrolyte;
3. obtaining reproducible agitation;
4. accurate measurements of electrode potential at high current densities;
5. build-up of ferric ions in solution.

The first three of these problems are best overcome by the use of a rotating cylinder electrode as the cathode.

Edge effects are reduced to a minimum because, firstly, two of the edges are removed by the use of a cylinder and, secondly, use of close fitting P.T.F.E. end caps effectively minimised the occurrence of nodular growth at the ends of the electrode. The rotating cylinder produces strong turbulent flow over its surface, this effectively solves the second and third of the above problems, since the turbulence breaks up the convection currents in the solution, and replaces them with powerful and reproducible agitation.

The modifications made to facilitate the accurate measurement of electrode potential have been described in the Experimental Section of this thesis. These are important as there is a rapid drop in potential with distance from the electrode, even in as conductive an electrolyte as the one under study especially when relatively large currents and hence high electric fields are involved. It is therefore of great importance that the potential sensing probe (Luggin) is situated in close and uniform proximity of the electrode.

Initial attempts to plate onto a titanium rotating cylinder of the dimensions given in the Experimental Section were not successful. Before a polarization determination could be made, it was necessary to preplate the electrode with a thin layer of iron ($\sim$ 10 μm thick) so that a fresh iron surface was present for deposition during the polarization run. However, attempts to produce an adherent preplated layer were entirely unsuccessful. Each time that an attempt was made to produce a layer of iron on the electrode, the deposit produced simply cracked and was peeled off the cylinder by the shearing forces of rotation.

The efforts made to overcome this difficulty are fully outlined in the Experimental Section of this work, and arose initially from consideration of the possibility of reducing the stress of the deposit as well as looking into different methods of surface preparation of the electrode to improve the adherence of the deposit. To reduce the stress acting in the deposit, the radius of the cylinder was increased to a maximum allowed by constraints of the neck size of the reaction vessel. This proved to be ineffective. Various methods of surface cleaning and etching failed to provide a solution to the problem, as did preplating at higher or lower current densities, and preplating deposits of reduced thickness in an effort to reduce the stress. The use of lower rotational velocities also failed to prevent the initial deposit from being removed from the electrode.

Attempts were then made to determine whether the deposit would adhere more successfully to other metal substrates. Rotating cylinder electrodes machined from stainless steel and nickel were tested, and iron successfully deposited onto them. This at least established a method by which the polarization characteristics of the electrodeposition of iron onto an iron surface could be studied and the characteristics in this electrolyte determined. Examples of the polarization curves that could be obtained are shown in Fig. 6.28. These were obtained on the stainless steel electrode. Similar data were obtained on the nickel electrode as would be expected, since in both cases the reaction under study is the electrodeposition of iron onto iron and not of iron onto the base substrate as this is covered by the initial galvanostatically deposited preplated layer.

Examination of Fig. 6.28 shows that a satisfactory polarization curve has been obtained up to a cathodic current density of 500 mA/cm^2, and that no evidence of the deposit fracturing is present. The most obvious feature of the curves shown in the figure are the limiting current plateaus in the potential range of approximately 500-800 mV (vs S.C.E.). The reason for the plateau is as discussed for the polarization curves shown in Fig. 6.20, that is, it is due to the reduction of ferric ions which build up in the solution as a result of the anodic oxidation of ferrous ions. In the case of the curves shown in Fig. 6.28, the magnitude of the current density at which these plateaus occur is much greater than those shown in Fig. 6.20. There are a number of reasons for this, firstly, the polarization curves shown in Fig. 6.20 were determined at a much lower temperature, 30°C compared with 100°C for those in Fig. 6.28. At a higher temperature the electrolyte undergoes greater oxidation by residual oxygen in the system, but more importantly, at the greater current densities involved in the latter determination, the quantity of ferric ion produced by anodic oxidation is obviously much higher. The final factor is the much increased rate of agitation afforded by the rotating cylinder electrode over the original arrangement of planar electrode combined with agitation by nitrogen diffusion.

In addition to the continuing problem of ferric ion build up, another major problem arises with the use of a stainless steel or nickel cathode, this is the fact that having achieved good adherence of the deposit to the substrate, the adhesion was so strong that it was not possible to peel the deposit from the cathode. This gave rise to considerable practical difficulties, as it is essential that there is a reproducible pure, oxide free iron surface from which to obtain polarization data. The best method of doing this was to deposit a layer of electrolytic iron from the solution under known conditions. If the iron deposited during polarization determinations cannot be removed with reasonable facility, then the preparation of a pure substrate for deposition becomes very difficult as iron is readily prone to surface oxidation, and the subsequent surface characteristics of the substrate are unpredictable and irreproducible. The most effective method for the preparation of a reproducible iron surface for the study of the system's electrochemical characteristics under these conditions would appear to be the 'in situ' deposition of a layer of iron produced in a controlled environment where the deposit produced is protected from the adverse effects of atmospheric oxidation.

To this end, it was essential that the problem of foil adherence to the titanium cylinder be overcome so that previous deposits could be removed and a good deposit of iron produced in preparation for the polarization determination. Further work in this area eventually provided the solution to the problem which was resolved by increasing the pH of the electrolyte from 0.5 to 1.00. This small increase in pH, leads to slightly reduced hydrogen evolution at the cathode and results in a more ductile iron deposit which adhered satisfactorily to the cathode during deposition but could be easily and cleanly removed at the end of each determination.

Satisfactory resolution of foil adherence problems permitted the use of the titanium electrode and reproducible polarization curves could be obtained up to a current density of 1000 mA/cm^2. (Figure 6.29). The only remaining limitation to general reproducibility being the build-up of ferric ions in the solution. However, at the higher current densities which are essentially unaffected by the ferric ion build-up, the essential features of the polarization data are consistent and a most interesting feature is that the curves show no sign of a limiting current density for the Fe^{2+}/Fe reduction reaction, even at current densities to more than double those used in the normal plating operation. The significance of this becomes apparent when considered in conjunction with the results of the conductivity studies showing the variation of conductivity with concentration (summarised in Fig. 6.15), where it can be seen that the conductivity of the ferrous chloride electrolyte increases as the concentration of the electrolyte is decreased. These results indicate that it may well be possible to reduce the concentration of the electrolyte and thus improve the conductivity without a serious penalty in terms of reduced rates of deposition as there is obviously some margin for a reduction in electrolyte concentration without moving into concentration polarization of the reaction in question.

Industrially, another important factor arises here, as it has been found (241) that for maximum foil ductility and hence reduced product damage, the operating temperature of the deposition process must be as high as possible, but that the solution must not be allowed to reach its boiling point as this would have an obviously detrimental effect on the product. The boiling point of a solution will change with change in solute concentration as follows:

$$\Delta T_{bP} = \left[\frac{RT_{bp}^{2}}{n_A \; \Delta H_{vap}}\right] m \quad \ldots\ldots\ldots \qquad \text{Equation 7.21}$$

where: T_{bp} is the change in boiling point;

R is the gas constant;

T_{bp} is the solution boiling point;

n_A is the number of moles of solute per 1000g of solvent;

m is the molality and ΔH_{vap} the heat capacity of evaporatic

From this it follows that a reduction in the concentration of the electrolyte will lead to a corresponding reduction in its boiling point, resulting in decreased foil ductility. However, it may well be possible to avoid this by the addition of suitable salts of the type discussed in the conductivity section of this work. Addition of these salts would lead to a further enhancement in the conductivity of the solution and since the boiling point of a solution is a colligative property, it will combat any tendency towards a reduction in the boiling point of the electrolyte.

As mentioned above, the major remaining problem in the establishment of reproducible polarization data, and a problem of significant industrial concern is the presence and build-up of ferric ions in the electrolyte. As can be seen in Fig.6.28 and Fig. 6.29 the concentration of this ion is giving rise to fairly large limiting current densities (20-100 mA/cm^2) for its reduction to its ferrous state.

Chemical analysis showed that this, was due to the presence of between 0.04-0.10 M ferric ion in the electrolyte.

As indicated in the polarization curves some of the current passed through the cell is in effect wasted in the reduction of ferric ion to ferrous ion. Therefore, one might expect a reduction in the cathode current efficiency of the process, if the ferric ion is not removed from the solution. This was found to be the case as is shown in Fig. 6.30. The current efficiency falls off sharply as the quantity of current passed through the solution increases and the ferric ion builds up. Figure 6.31 gives an indication of the corresponding build-up of ferric ion in the electrolyte, increasing from 0.04 M in the freshly made up electrolyte to approximately 0.10 M, where a degree of equilibrium is reached between the production of ferric ion at the anode and its reduction at the cathode.

In the industrial operation the ferrous ion concentration is restored and the ferric ion concentration reduced by chemical dissolution of scrap iron in hydrochloric acid, and although the oxidation potentials of the relevant half-reaction (Appendix I) indicates that ferric ion should be reduced to ferrous ion, the kinetics of the reaction are such that the ferric ions tend to be hydrolysed to form a brown, colloidal precipitate. Practical experience has shown that some of this colloid tends to resist the regeneration process and is recirculated to the electrolytic cell adversely affecting the current efficiency and occasionally becoming included in the deposit. The inclusions give rise to defects in the thin foil such as pinholes and are clearly undesirable. An example of the defects caused by the inclusion of hydrated ferric oxide particles is shown in the scanning electron micrography (Appendix II). Clearly, this is a further reason for minimising the ferric ion concentration in the electrolyte.

As stated, regeneration of the 'spent' electrolyte with scrap iron and hydrochloric acid was only partially successful in removing the solid hydrated ferric oxides. A number of methods of chemical reduction of the electrolyte were considered as possible solutions to this problem, but the majority were rejected on grounds of introduction of foreign metal ions into the electrolyte and/or cost, e.g. use of tin (II) as a reducing agent. However, one strong reducing agent that fulfilled the required criteria remained. This was aqueous hydrazine. The major advantage of hydrazine in its use as a reducing agent is that its reaction products are innocuous, being nitrogen and water. Another notable advantage particularly in the laboratory cell is its ability to remove dissolved oxygen from the electrolyte, minimising further oxidation of ferrous ion by this species.

The initial attempts to reduce the ferric ions in solution were made with aqueous hydrazine i.e. hydrazine dihydrate ($NH_2NH_2.2H_2O$). This derivative, while partially effective as a reducing agent as evidenced by a change in colour of the bulk of the solution to a clear green, also caused the formation of a gelatinous precipitate. This was probably due to the basic nature of aqueous hydrazine causing the formation of basic ferric hydroxides. Polarization determinations carried out in solutions reduced in this fashion e.g. Fig. 6.32 show that the Fe^{3+}/Fe^{2+} limiting current density has fallen to about 3 mA/cm^2 from previous values of about 20-30 mA/cm^2 as in Fig. 6.29. The results shown in Fig. 6.32 also indicate that on successive runs, the ferric ion level increased showing that the hydrazine did not continue to reduce the ferric ions after the initial addition. It was not possible to determine what proportion of the hydrazine was involved in the reduction reaction and what was involved in the precipitation reaction, therefore the stoichiometry of the procedure could not be determined. Various attempts to overcome the precipitation of the hydroxides on hydrazine addition proved unsuccessful, addition with vigorous agitation, addition of more dilute solutions of hydrazine, and addition at various temperatures all proved ineffective.

The problem was overcome by the use of an acidic derivative of hydrazine, hydrazine dihydrochloride ($N_2H_4.2HCl$). This derivative does not increase the pH of the electrolyte and thus the problem of hydroxide precipitation does not occur. The use and effects of this derivative on the deposit has been cited in the literature(242-244) from which further details may be obtained.

The use of hydrazine dihydrochloride in the laboratory cell proved to be highly effective in the chemical reduction of ferric ions. As shown in Fig. 6.33, it reduces ferric ions on an almost stoichiometrical basis, the relevant half reactions being: $Fe^{3+} + e^- = Fe^{2+}$ ..... Equation 7.22

$N_2H_4.2HCl + 4OH^- = N_2\uparrow + 4H_2O + 2HCl + 4e^-$ " 7.23

In the deoxygenated electrolyte, protected from atmospheric oxidation by a blanket of nitrogen, 0.1 M levels of ferric ion were reduced by a factor of three within an hour of the hydrazine dihydrochloride addition. Once reduced to this level, there was a further slow decrease over an eighteen hour period, probably indicating that ferric ions locked up as solids in the solution are slowly coming into solution and being reduced. It also indicates quite clearly that most of the oxygen remaining in solution even after scouring with nitrogen has effectively been mopped up.

To try to simulate the industrial case more closely the procedure was carried out using a solution open to the effects of the atmosphere. The result, also shown in Fig. 6.33, again indicates that this reducing agent is effective under these conditions. The rate of chemical reduction is slightly diminished, and the overall extent of the reduction is not as great as in the nitrogen protected electrolyte, but the difference is not large ($\sim$ 0.005 M), and could possibly overcome by an increase in the quantity of hydrazine dihydrochloride used. The major difference between the two sets of conditions is that the ferric ion concentration in the electrolyte subjected to a normal atmosphere began to increase slowly after four or five hours. This is most likely due to the fact that the reducing agent has been exhausted and the electrolyte is slowing taking up atmospheric oxygen which oxidises ferrous ions in solution.

The results described in Fig. 6.33 are concerned merely with the reduction of ferric ions in a 'static' bath. It was considered important to attempt to elucidate the reduction characteristics of hydrazine dihydrochloride in the dynamic system. The outcome of this determination is shown in Fig. 6.34. The ferric ion concentration rose quite rapidly once the deposition process was started, as this concentration approached an equilibrium value a stoichiometric equivalent of the dihydrochloride was added. The ferric ion concentration declined in a similar fashion to static reduction experiment, but the decrease was notably reduced, in this case only approximately 0.02 M, compared with approximately 0.07 M. However, it is important to note that the hydrazine dihydrochloride is able to reduce the ferric ions more rapidly than they are produced at the anode during a plating operation at the stated current density. As before, larger quantities of the compound could be used to produce a greater reduction in the ferric ion concentration.

This operation, while successful within the circumstances described, would in an industrial plant probably be performed either in the regeneration system or in a separate tank. Thus the ferric ions produced at the anode may well still prove to be problematical in the electrolytic cell, where they may be immediately transferred to the cathode surface while still in the cell. If the inclusion of these particles in the deposit is to be reduced to an absolute minimum, as is the requirement for a 'pore-free' thin foil, then methods of preventing the transfer of ferric ions across the electrode gap must be considered. It is also worth recalling that from the academic stand point the build-up of ferric ions in the catholyte is undesirable as it seriously affects the degree of reproducibility that may be achieved.

Divided Cell

In the usual method of continuous foil electroforming on a slowly rotating cylinder with the electrolyte cascading through the inter electrode gap, the streaming effect of the fast flowing electrolyte does to some extent reduce the transfer of ferric ions across the electrode gap. However, this effect alone is insufficient to entirely remove the ferric ions from the catholyte. It was therefore apparent that for the laboratory system some type of physical or physio-chemical barrier was necessary between the cathode and anode.

A cationic ion exchange membrane was chosen as most suitable for the laboratory cell. Chemical analysis of the catholyte during the plating process showed that there was no discernable increase in the ferric ion level over a number of hours (Table 7.3), indicating that the membrane was functioning in the desired manner. As would be expected there was a significant increase in the ferric ion concentration in the anolyte of the laboratory cell since no regeneration procedure was explored. In industrial practice, the anolyte would be recirculated for regeneration.

The incorporation of a membrane into an electrolytic cell is done at the expense of increased power requirements, as the membrane adds to the electrical resistance of the current path in the cell. Figure 6.35 gives some indication of the extent of the ohmic losses in the laboratory cell in terms of increased cell voltage requirements when the membrane was used. Simple ohmic considerations show that the cell resistance is increased by some 30%. While this factor is not of great significance in the laboratory, it is of paramount importance in an industrial environment, where costs must be kept under careful scrutiny.

The concept of a divided cell has been shown to be effective in overcoming some of the problems associated with this type of operation, and in the absence of suitable alternatives may prove to be a price that must be paid if a defect free product is to be produced. An alternative which should be considered, but whose properties have not been explored during the course of this project, is the use of a diaphragm between the anode and cathode. This would provide a purely physical method of cell division which would serve to keep any particulate hydroxides formed at the anode away from the cathode. A diaphragm of this nature would be porous and may well prove to be a smaller impediment to electrical conductance than an ion exchange membrane.

In addition to demonstrating that an ion exchange membrane could be an effective solution to some of the problems encountered, the divided laboratory cell provided a satisfactory system for the investigation of some of the characteristics of the deposition procedure. The first of these was to determine the cathode current efficiency (C.C.E.) of the process with a minimum amount of ferric ions in the electrolyte. The results obtained at a number of cathode current densities shown in

Table 7.4 indicates that the C.C.E. is greater than 98 ± 0.3% and is constant if ferric ions are not allowed to build up in the catholyte. They also indicate that up to a current density of 5000 A/ m^2, the current efficiency of the process is constant and not a function of current density. This is significant as it means that hydrogen evolution at these current densities and potentials is minimal, although it would appear to account for approximately 1-2% of the current used. Determination of the cathodic current efficiency at various rotational velocities (Table 7.5), indicates that this parameter has no discernable effect on the current efficiency within the range shown. From this observation it may be inferred that rotational velocity of greater than 200 rpm in this system is sufficient to provide an adequately turbulent regime so that hydrogen formed on the surface of the deposit is quickly swept away.

The incorporation of the membrane also meant that reproducible polarization curves could be obtained. A typical example is shown in Fig. 6.36. Only one curve has been illustrated in this figure since the results of successive runs done to establish reproducibility could essentially be superimposed on the result of the first determination. The polarization curve displays a slight point of inflexion at low current densities (20-30 mA/cm^2) probably due to the presence of a small concentration of ferric ion not removed by the described pretreatment. This was not completely unexpected as due to the practical limitations of the available equipment it would be unrealistic to expect a 100% reduction of ferric ions. Unless very sophisticated and expensive facilities and techniques are available for handling and treating the electrolyte, then there will always be minute quantities of dissolved oxygen and contaminants present, giving rise to ferric ions in the solution. The important consideration from this result is that once a minimum level of ferric ions had been achieved it could be held constant. It is then possible to determine the effects of other variables on the polarization characteristics.

Use of surfactants

It was considered that the addition of a surface active agent (surfactant) to the electrolyte might lead to enhanced polarization characteristics. It may act as a wetting agent at the electrode/electrolyte interface and be beneficial in removing gas and depolarizing gas films. It may also aid in the removal of ferric hydroxide particles or additive by products by adsorbing onto particles to provide a negatively polarized shell which would be repelled from the cathode thus decreasing the chances of inclusion into the deposit.

Examples of the three major classes of surfactants (cationic, anionic and non-ionic) were chosen on their ability to withstand the rigours of the aggressive acid chloride electrolyte, and their non-foaming or stable foam producing characteristics. The latter point being an important consideration in the industrial environment where excessive foaming could be highly undesirable.

The results of the cathodic polarization determinations in the electrolyte with various additions of surfactant

(Figs. 6.38-6.40), did not however, indicate any significant improvements. The polarization characteristics after the addition of the cationic and anionic surfactants (Figs. 6.38 and 6.40) showed some small tendency towards depolarization at current densities greater than approximately 60 mA/cm^2. These changes were less than 10% and are within the limitations of experimental reproducibility and cannot be considered as significant. The addition of a non-ionic surfactant did not result in any modification of polarization characteristics, as Fig. 6.39 indicates there are minor differences in the curves at lower current densities due to different initial concentrations of ferric ion, but at higher current densities where the effect of ferric ion ceases to play a significant role, the curves are identical for various concentration of surfactant. The ionic surfactant used 'Texofor N.12' ABM Chemicals Limited exhibited undesirable foaming characteristics particularly at the higher levels of addition (> 0.2%). Excessive quantities of light and unstable foam were produced which would make the use of this surfactant in this application inappropriate even if it was found to be in some way beneficial.

It was not possible to apply these surfactants to production or pilot plant tests, where their benefits and shortcomings could be examined under more realistic conditions. Thus no comment can be made on their effect on the incidence of particle inclusions in the foil, nor can a realistic estimate be made of their lifetime in the electrolyte during production, or to the effects of possible degradation products. In the laboratory they were found to remain effective for the duration of the useful life of the test electrolyte.

Theoretical Considerations

No attempt has been made, nor would be possible, to discern or establish details of the reaction mechanism for the iron deposition process from the potential-current relationships observed in the electrolyte under the conditions studied. The mechanism of iron electrodeposition has been rigorously studied by Bockris et al and has been summarised by Bockris and Conway(181). Highly specialised facilities were required to ensure the complete absence of ferric ions and for the preparation and preservation of completely pure and reproducible iron surfaces. It was necessary to measure very small amounts of H_2 e.g. 10^{-8} moles, and to accurately determine pH changes at the electrode/electrolyte interface. In addition, this type of work necessitates the use of low concentration solutions such as 0.05 M, so that ionic interactions may be minimised. Such a study is academically sound but of course not realistically representative of an industrial electroforming process.

The electrolyte under study during this project was operated at high temperature, low pH and high concentration since it was developed for industrial operation at high rates of deposition. The apparatus involved was developed as a compromise between a laboratory simulation of industrial conditions and the more stringent demands of obtaining accurate academic information of a large scale industrial process. It was not developed to undertake the study of the mechanism of deposition processes, and as such will not facilitate the complete removal of ferric ions which will affect the lower end of the Tafel region. The effects of hydrogen evolution from the acidic electrolyte would also interfere with the Tafel characteristics. It is therefore, clear that given this electrolyte and the nature of the studies conducted, it would be unrealistic to attempt to comment on the precise mechanism of the reaction process.

VIII CONCLUSIONS

(i) Pilot Plant Studies

The major practical conclusions arising from the operation of the plant are outlined in Chapter IV, Section v. In more general terms, the study acted as confirmation that the process is a difficult one to operate and control. Factors such as solution oxidation, and difficulties in pH and ferric ion control necessitate careful monitoring and adjustment of electrolyte parameters.

(ii) Electrical Conductivity of the Electrolyte

There would appear to be little margin for improvement in the electrical conductivity of an almost saturated (3.5 M) ferrous chloride electrolyte. However, significant improvements could be made if the concentration of the electrolyte was reduced. A reduction from 3.5 M to 1.5 - 2.0 M might be appropriate and this would not seem to otherwise restrict the rate of deposition.

Addition, or the increase in concentration of a 'conductivity salt' to a ferrous chloride electrolyte of reduced concentration would serve to improve the electrolyte conductivity. Two suitable examples, which are also economically viable, are sodium chloride and ammonium chloride, the latter being superior for conductivity purposes. Concentrations within the range 0.5 - 1.0 M for sodium chloride and 1.0 - 2.0 M for ammonium chloride could be recommended.
- ionic strength remains similar to 3,5 M ferrous chloride alone and boiling point - unchanged

The combination of reduced ferrous chloride concentration and the addition of the 'conductivity salts' at the level suggested means that the ionic strength remains similar to 3.5 M ferrous chloride alone, and the boiling point of the electrolyte will be virtually unchanged.

(iii) Anodic Polarization and Anodes

This section of the work indicated that the graphite anode already in use is indeed the most practical choice for this application. Materials such as the platinised titanium anode tested which showed desirable polarization characteristics, may become increasingly important in this application once their physical characteristics have been developed to the extent where they can survive the aggressive environment produced by this electrolyte.

(iv) Cathodic Polarization

The limiting current density for deposition from the concentrated iron chloride electrolyte appears to be very large. From the electroforming standpoint it is not a limiting factor as nodular growth at the edges of the foil occurs and prevents the production of high quality foil at current densities above 4000 - 5000 A/m^2.

One positive benefit of this result arises from consideration of the conductivity data, where it has been indicated that a lower concentration may be advantageous because of increased conductivity. The results of the cathodic polarization studies indicate that the ferrous chloride concentration could to some extent be reduced without a detrimental effect on the polarization characteristics in terms of reduced deposition rate. Further work is necessary to determine the extent to which the concentration could be reduced without serious penalty.

Studies in this area also indicated that the Fe^{2+}/Fe^{3+} redox reaction is a major determinant in the electrolyte stability for both short and long term electrodeposition. Any attempts to produce high quality iron electrodeposits from the ferrous chloride electrolyte must take this parameter into account and must consider methods for the minimisation of the ferric ion concentration.

(v) Minimisation of Ferric Ion Concentration

It is desirable to eliminate as far as possible ferric ions from the catholyte. This may be achieved by three possible approaches:

(a) External regeneration of ferrous ions by reduction of residual ferric ions. At present chemical dissolution of scrap iron is used to replenish iron in solution and does so at the expense of hydrochloric acid without much reduction of ferric ion in solution, i.e.

The major reaction is: $Fe + 2HCl \rightarrow FeCl_2 + H_2$

and not: $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

The Fe^{3+}/Fe^{2+} redox reaction might be more complete if an electrolytic cell was established in the regeneration circuit for which a controlled potential and relatively low current would suffice.

(b) Chemical dosing of the solution at either periodic intervals or by continuous addition of a suitable reducing agent. This can be achieved using hydrazine (N_2H_4) which has the additional virtue of yielding innocuous reaction products but has a disadvantage in causing local precipitation when added in an uncontrolled manner as the hydrate. Hydrazine has been found to be effective but not on a strictly stoichiometric basis. Hydrazine is also available commercially as dihydrochloride which is a much more suitable form for use in this application since it does not give rise to precipitation of basic hydroxides. Clearly the use of this reagent is advantageous to the use of tin or cerium in this application.

(c) Introduction of a membrane or diaphragm, thereby separating the catholyte and anolyte, effectively prevents the anodic products from approaching the cathode surface and interfacing with the deposition process. Although the ferric ion concentration may build-up in the anolyte this will not be too inconvenient although the oxygen evolution level may increase.

Experimental work suggests that it is a very effective way of improving cathode behaviour.

An ion exchange membrane (cationic IONAC MC-3470) was used in this work but it is possible that a simple diaphragm might be adequate and if so would be economically favoured. If such a diaphragm/membrane were used it would have important implications for the engineering design of the plant, particularly in respect of replacement and maintenance.

(vi) Use of Surface Active Agents

The use of surface active agents in a highly agitated electrolyte appeared to have little effect on polarization characteristics i.e. it did not appear to aid removal of gas from the deposit surface. The effect of surface active agents or the incorporation of non-metallic material in the deposits was inconclusive.

(vii) Suggestions for Further Work

The major area requiring further investigation would be the implementation of many of the ideas generated from the laboratory studies, on an operational iron foil production plant. It was initially hoped that this would have been the case, however, plans to operate the iron foil plant at the Arthur Lee Group (Sheffield) were thwarted by their decision to decommission their plant.

Had the plant been available, it would have been useful to examine the production of iron foil from an electrolyte modified to improve its conductivity and to control the ferric ion concentration. It would also be interesting to determine the effects of the use of a divided cell in large scale production and to conduct a more thorough study on the use of surfactants, particularly as a method of diminishing the extent of inclusion of non-metallic material in the deposit.

Finally, it is necessary that the working limits of the solution should be defined more precisely, especially in the area of the electrolyte concentration.

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FIG. 3.1 Original Anaconda Rotating Drum Cell.

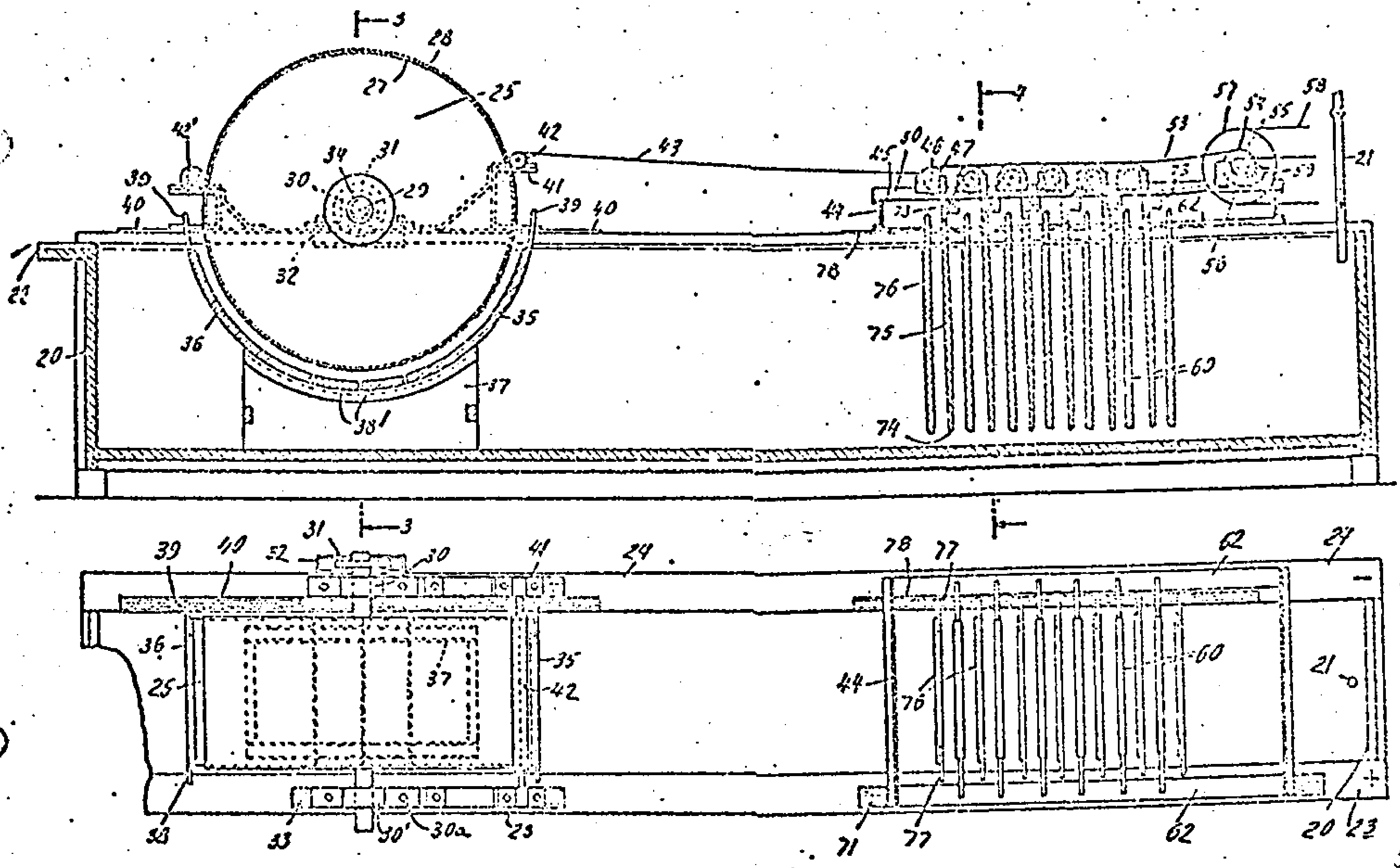


FIG. 3.2 Improved Anaconda Cell - Showing Installation of Tapered Roll.

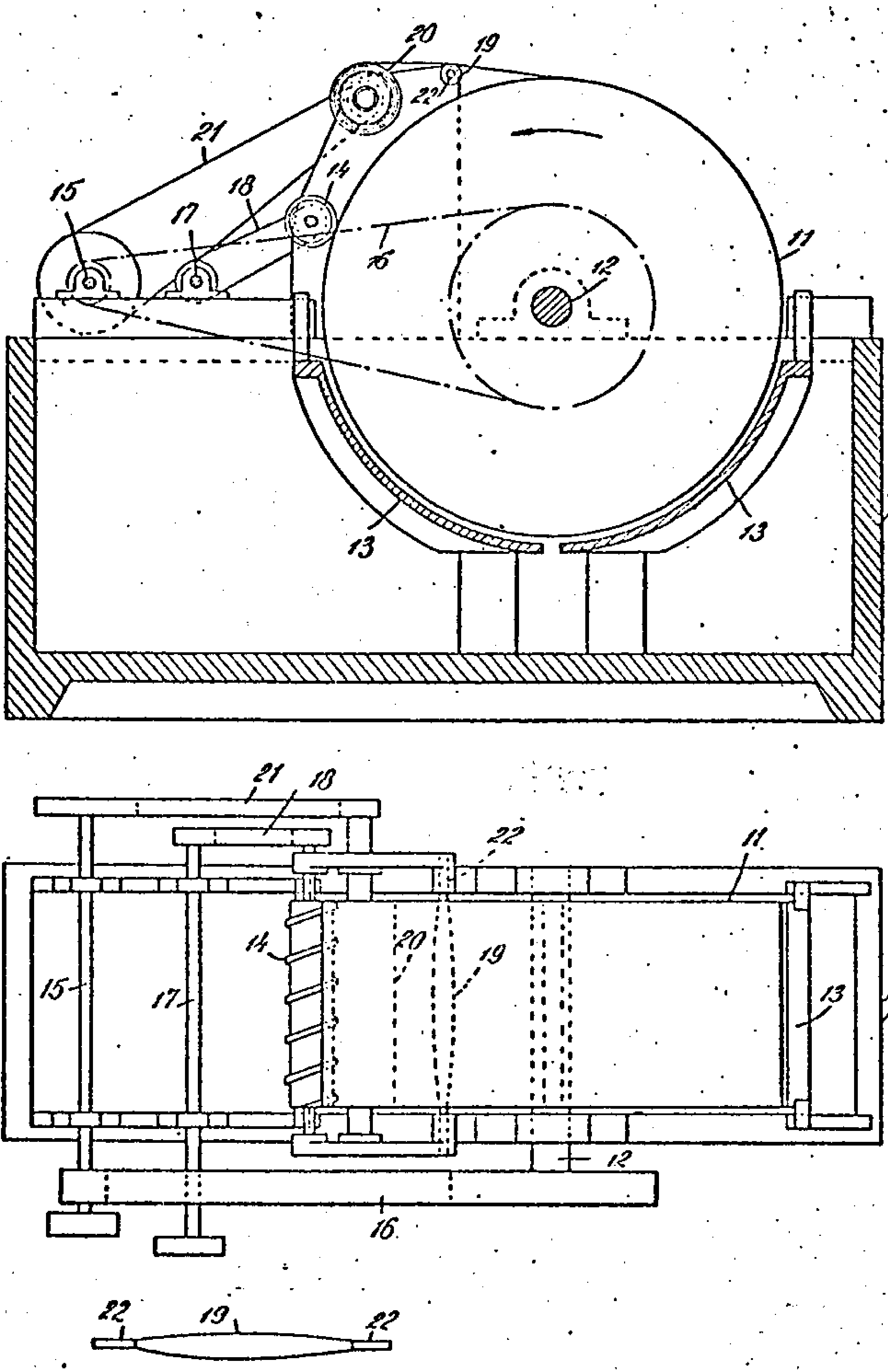


FIG. 3.3. Further Modified Anaconda Cell - Showing Novel Electrolyte Inlet.

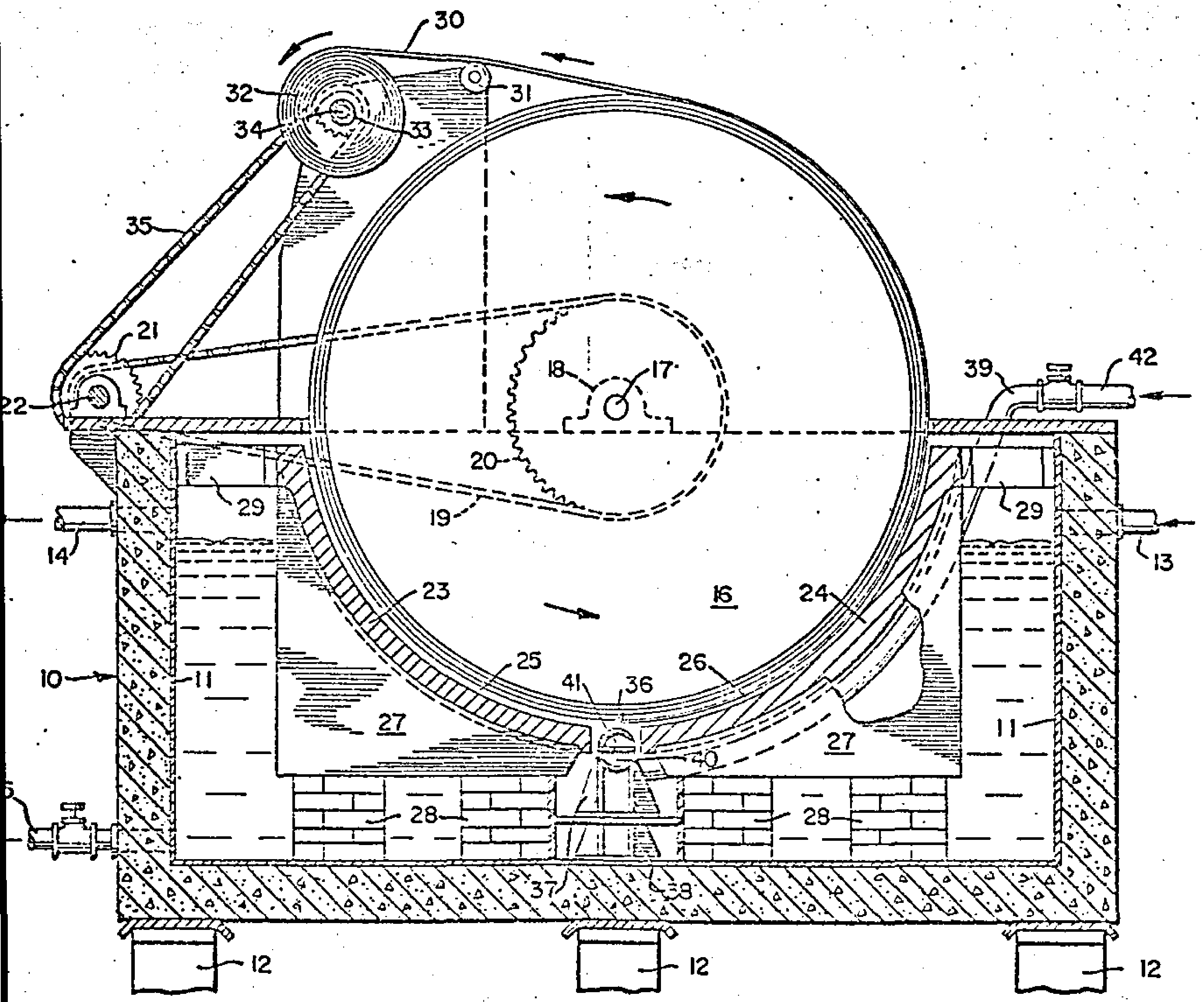


FIG. 3.4. Endless Band Cathode due to Pedone.

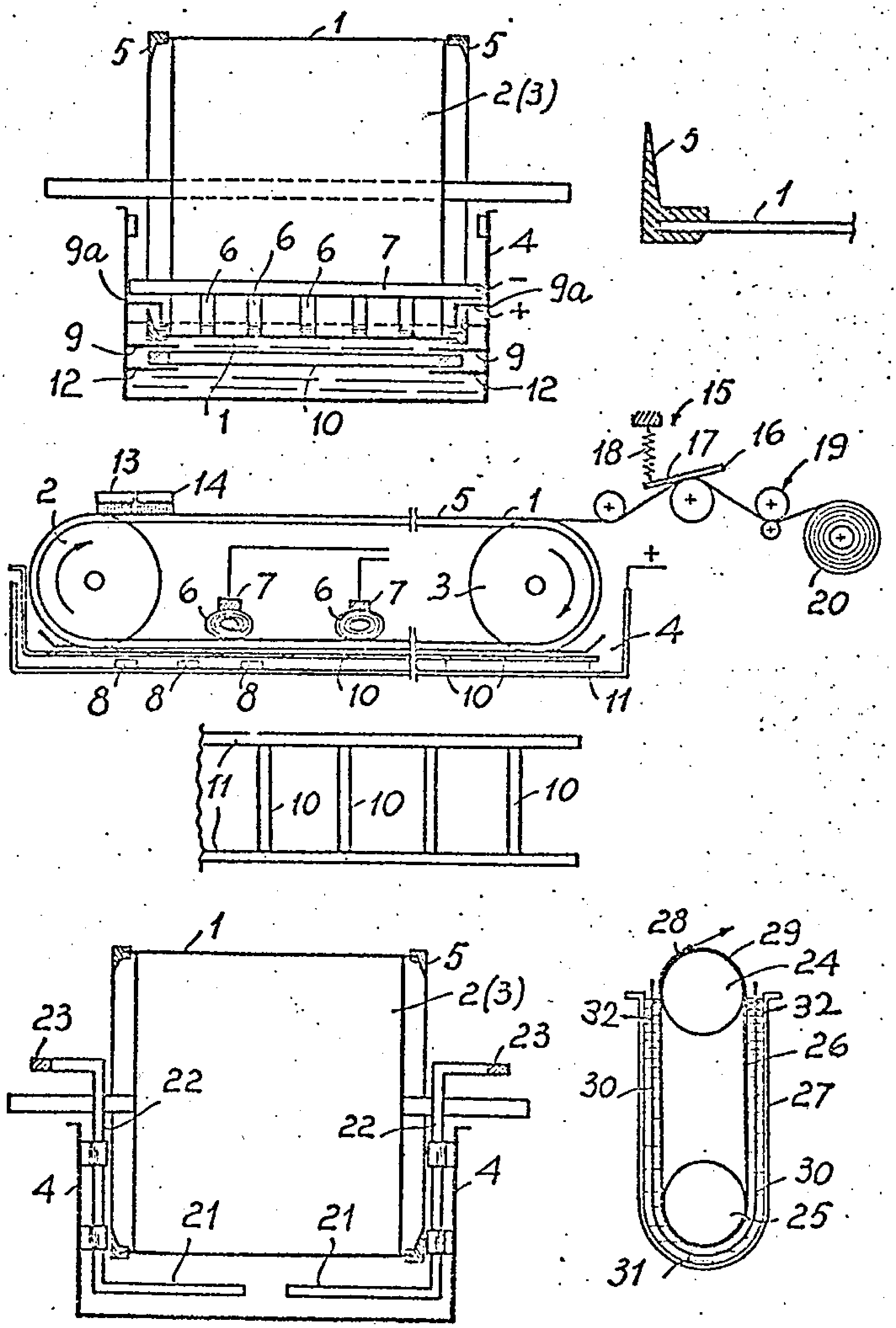


FIG. 3.5. Cell Design for Increased Current Efficiency.

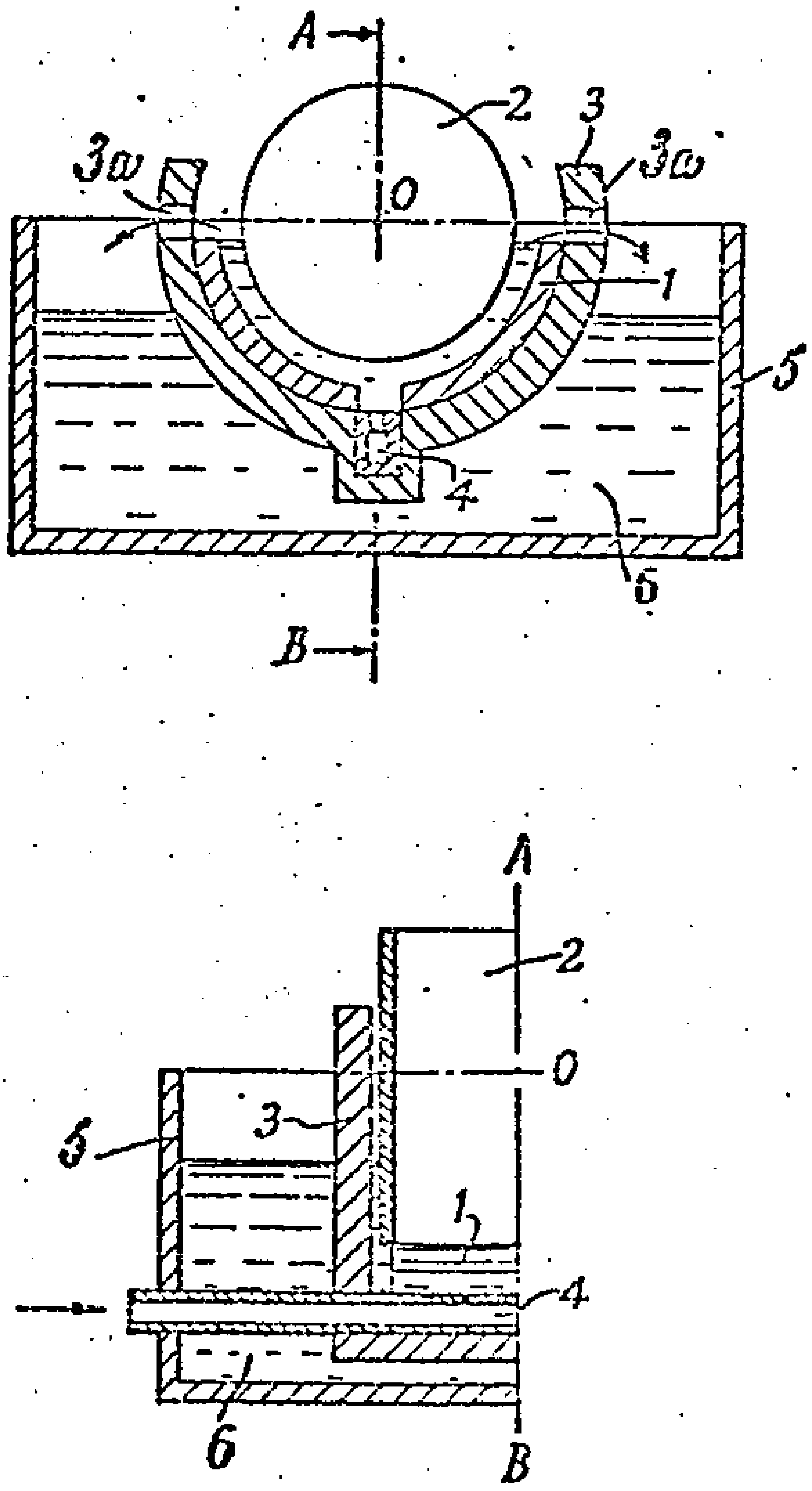


FIG. 3.6. Anaconda Titanium Clad Rotating Cylinder Cathode - Front View.

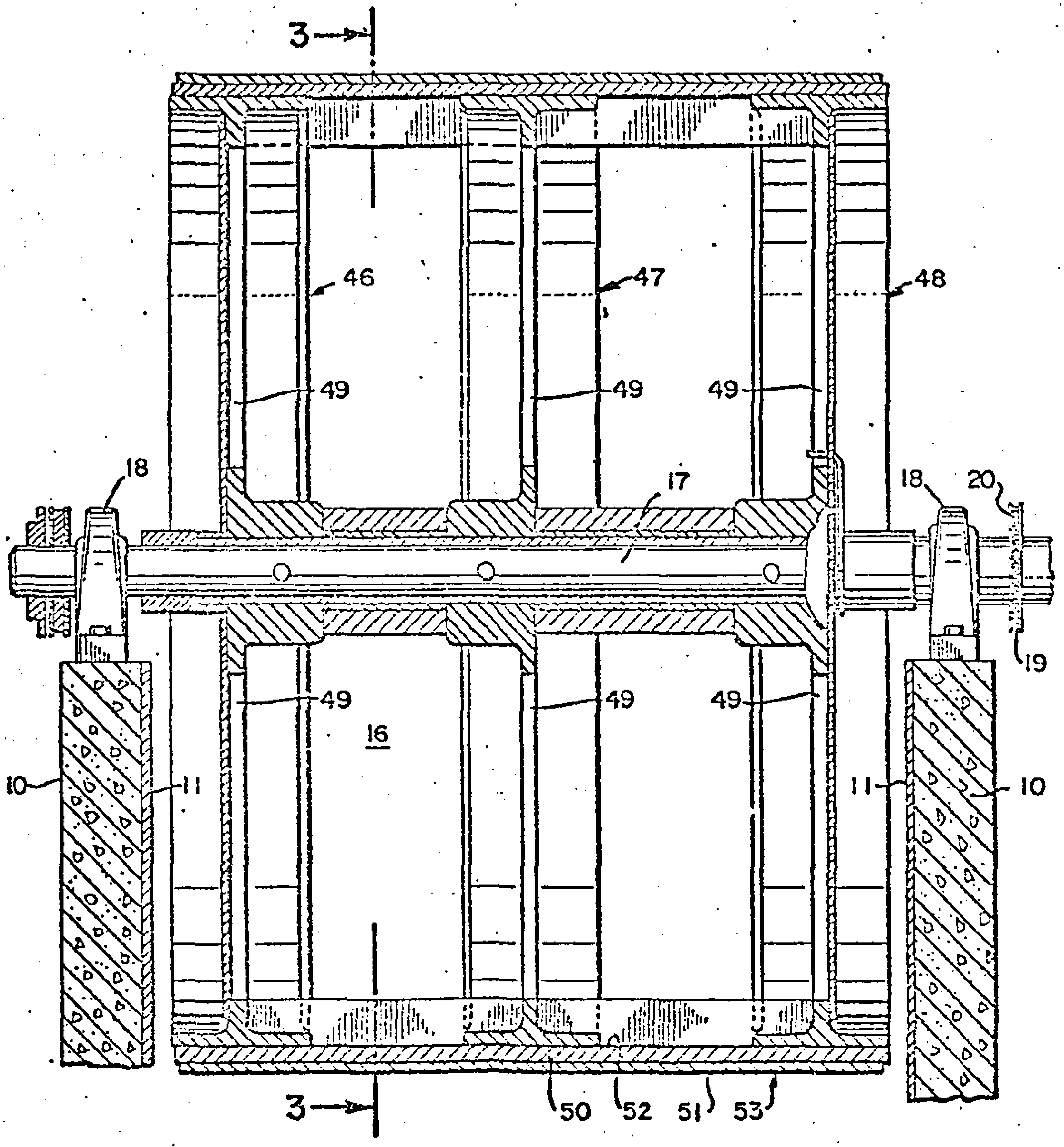


FIG. 3.7. As Fig. 3.6. - End View.

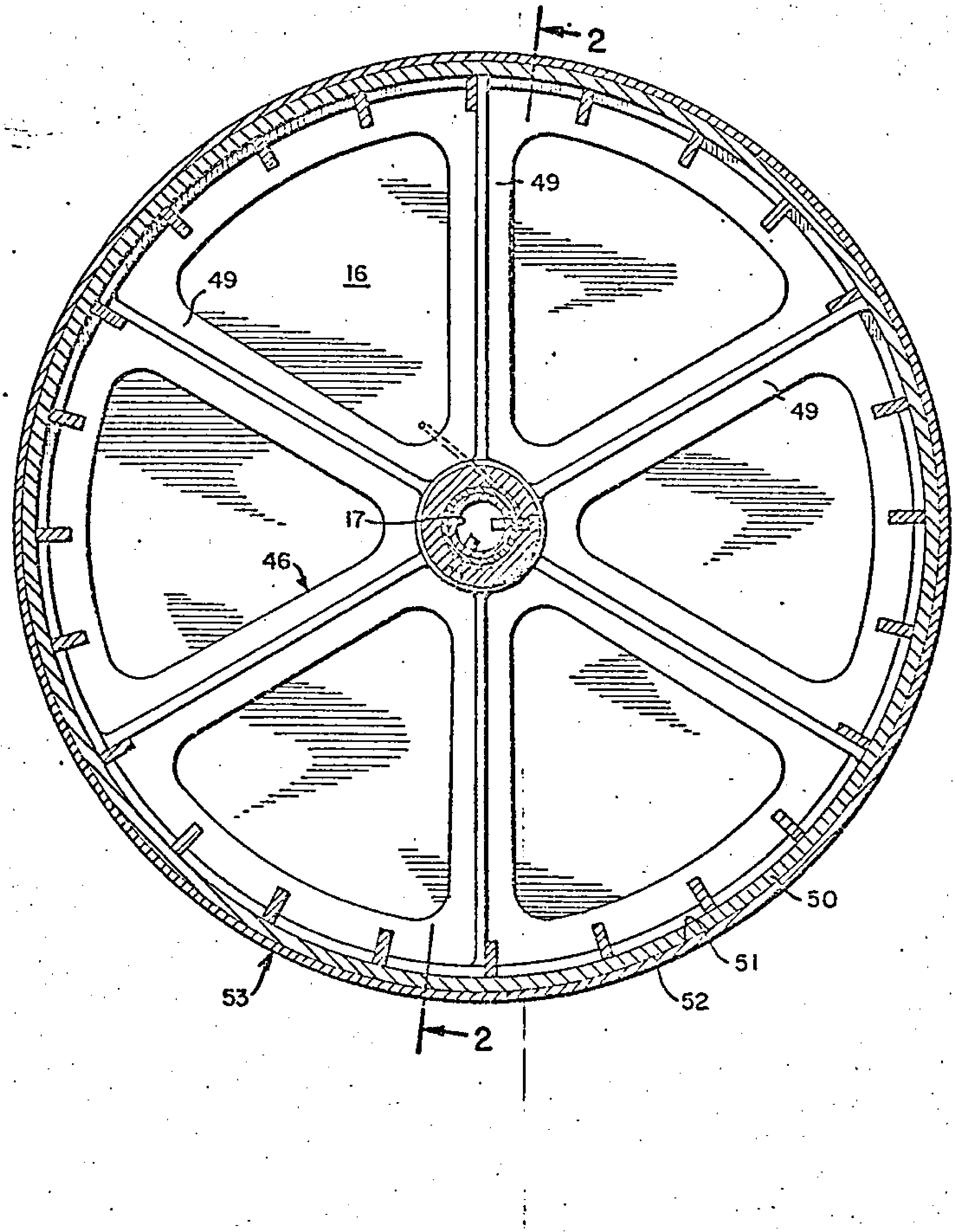
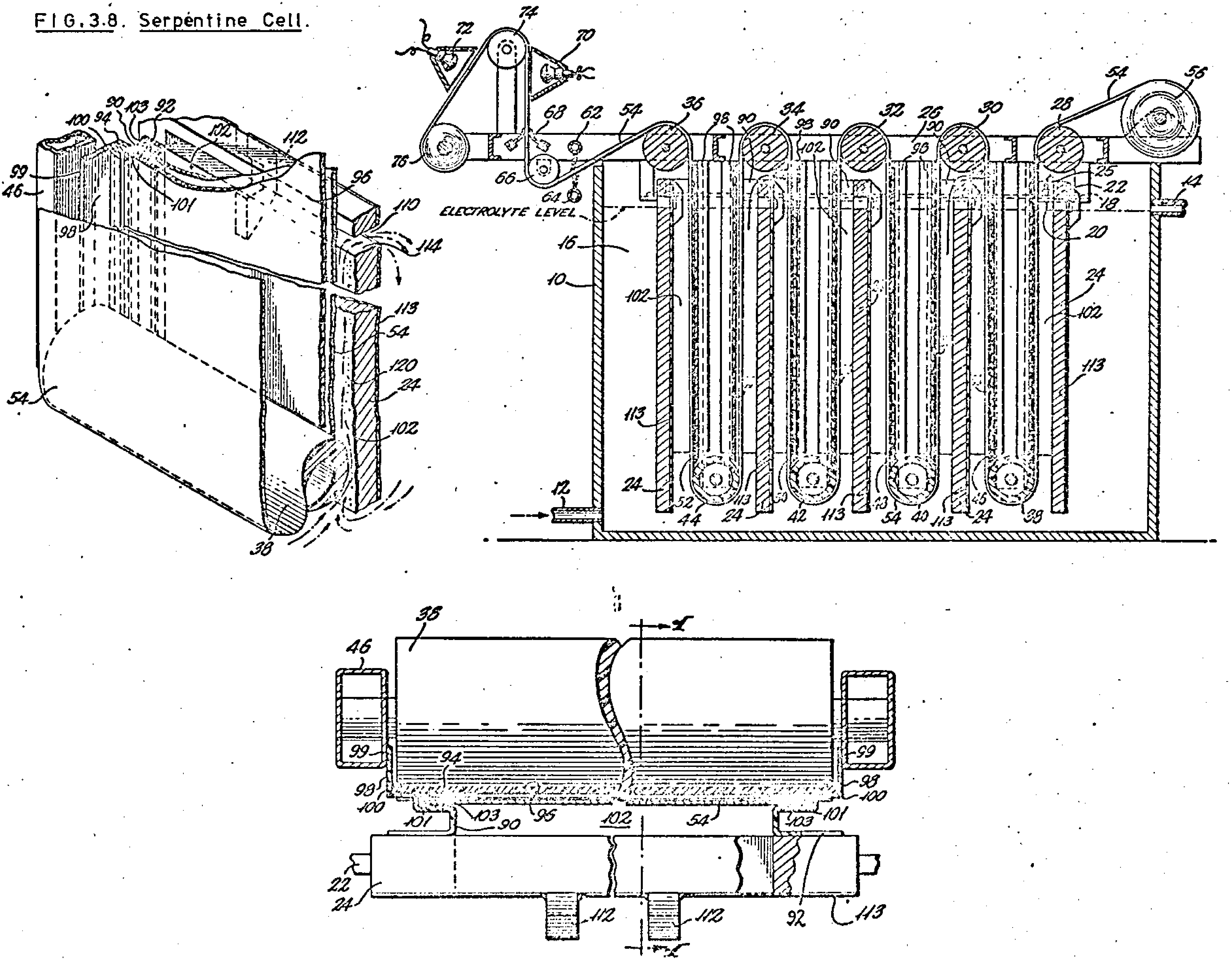


FIG.3.8. Serpentine Cell.



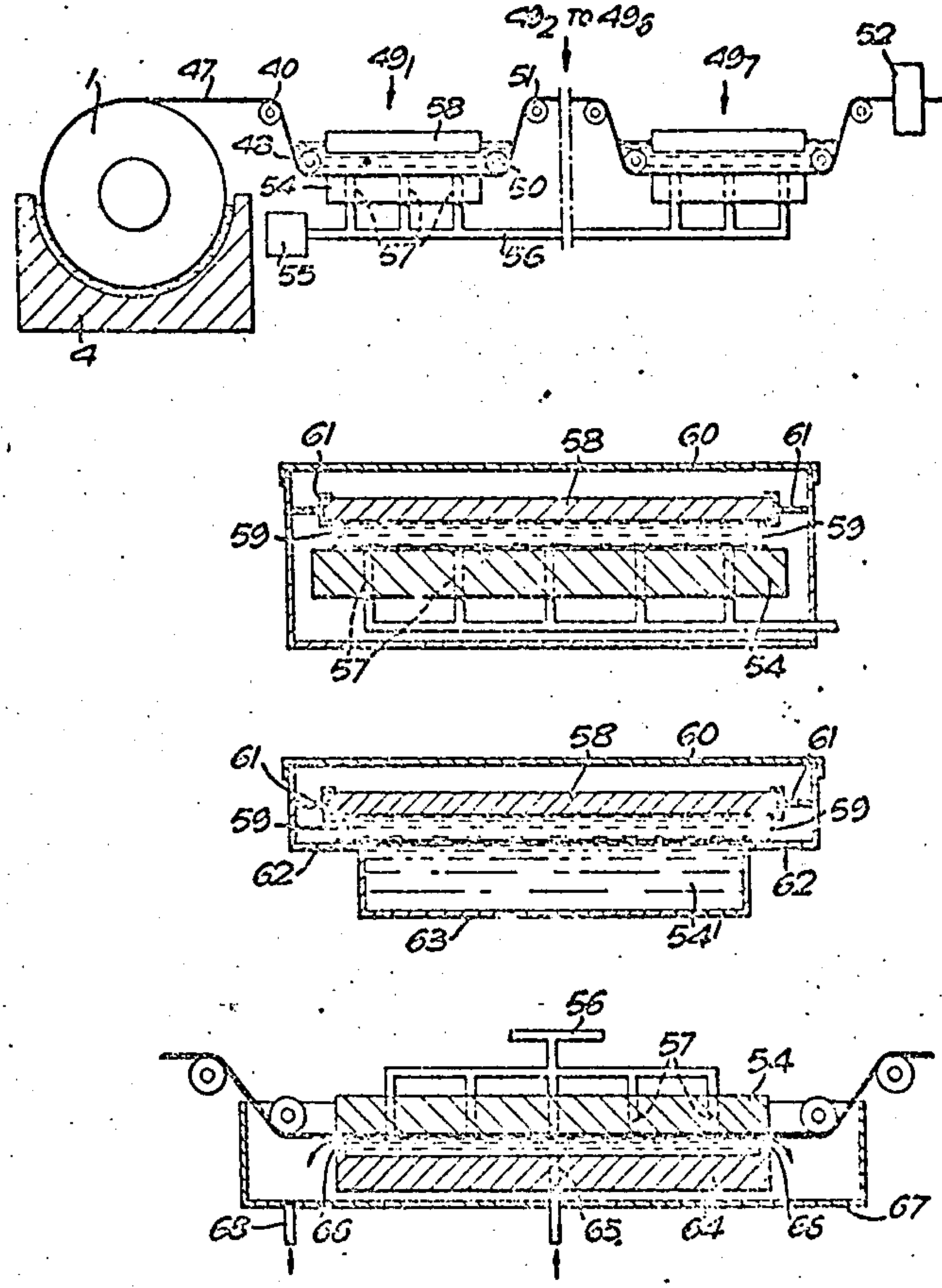


FIG. 3.9. Cell Designed to Maximise Foil / Current Scource Contact Area.

FIG. 3.10. Rotating Cylinder Cathode Cell with Moving Consumable Anode.

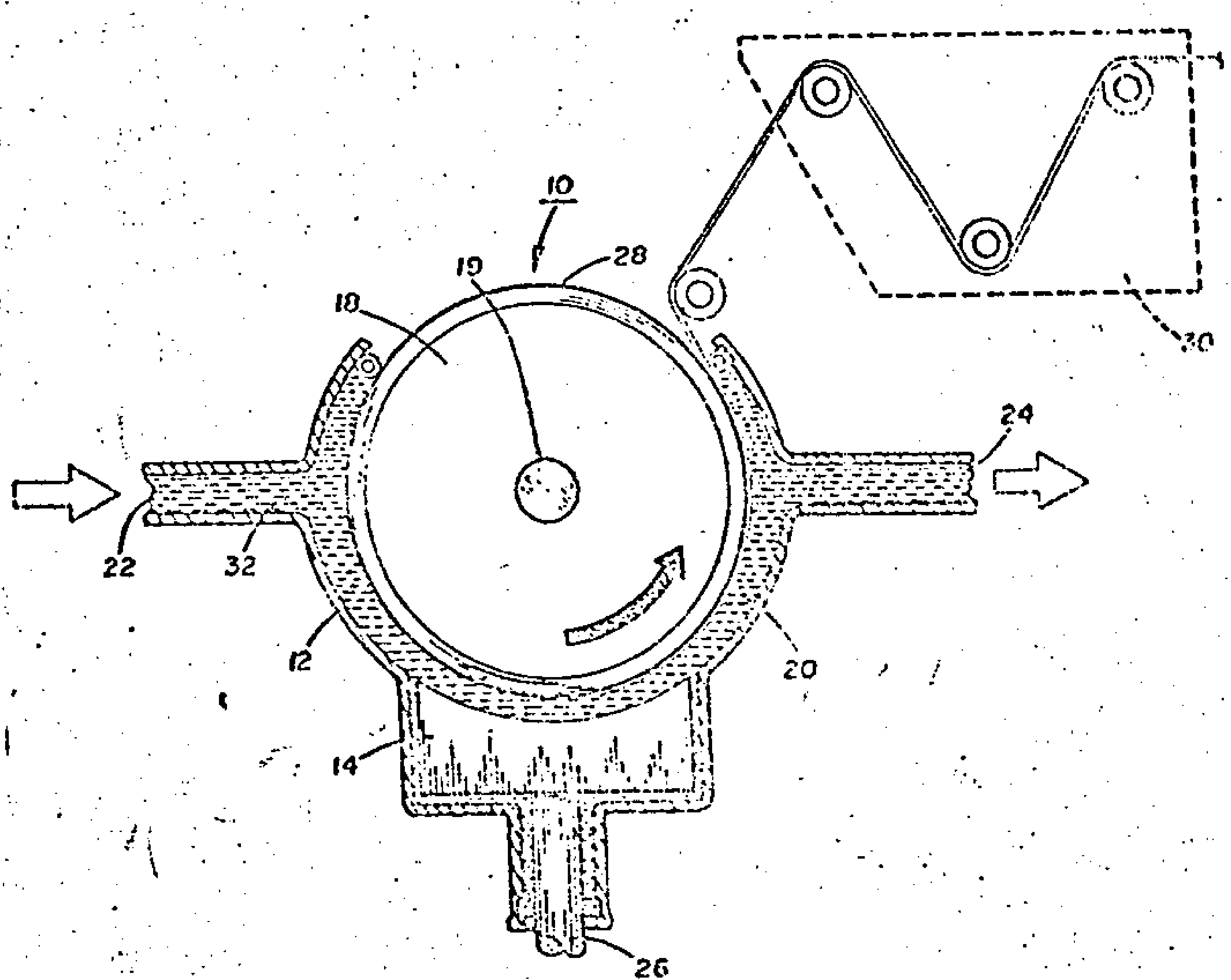


FIG. 3.11. Cell Design Showing Use of Consumable Anode in Conjunction with Melded Fibre Belt.

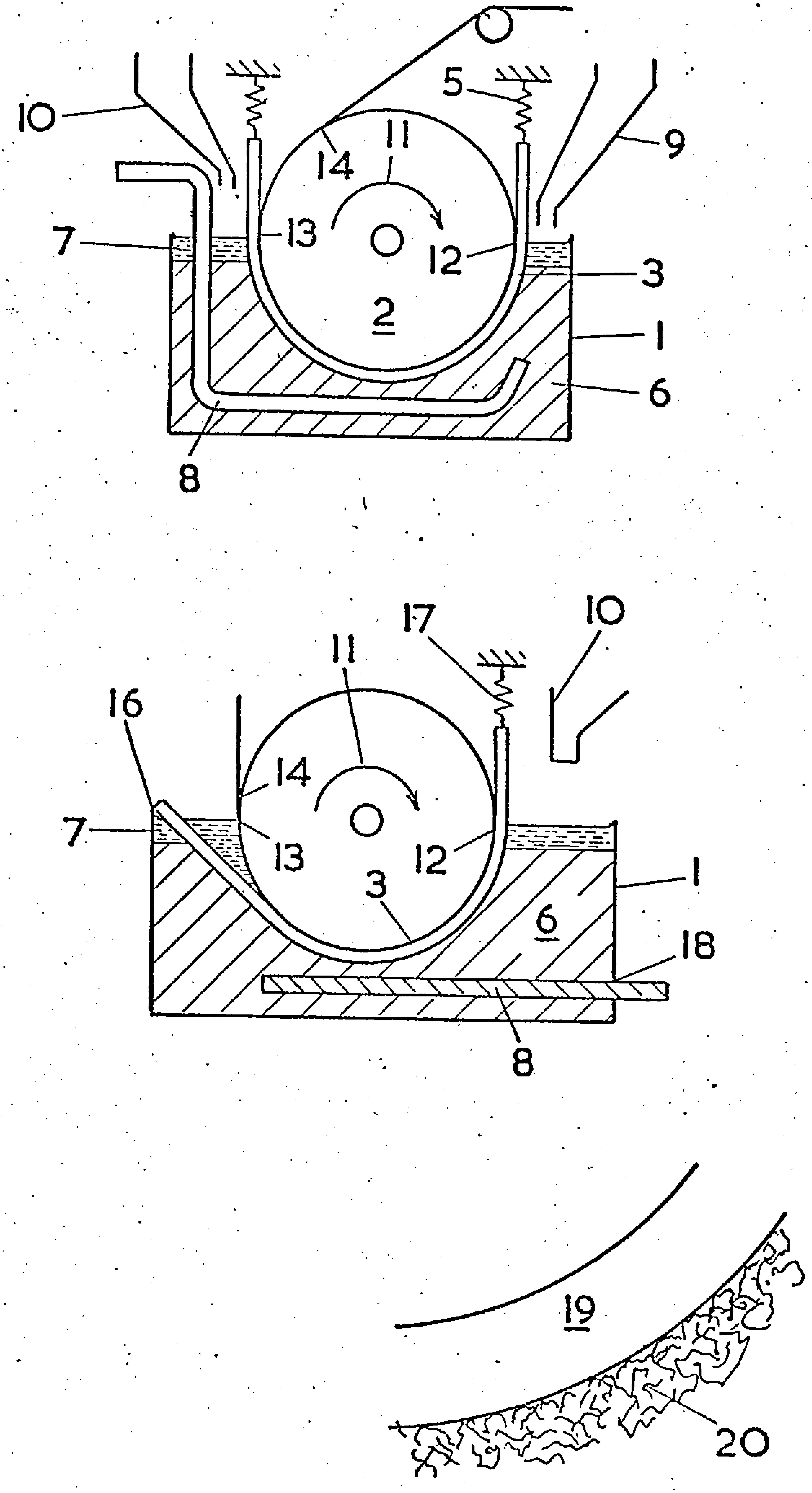


FIG. 4-1. Schematic Representation of Pilot Plant.

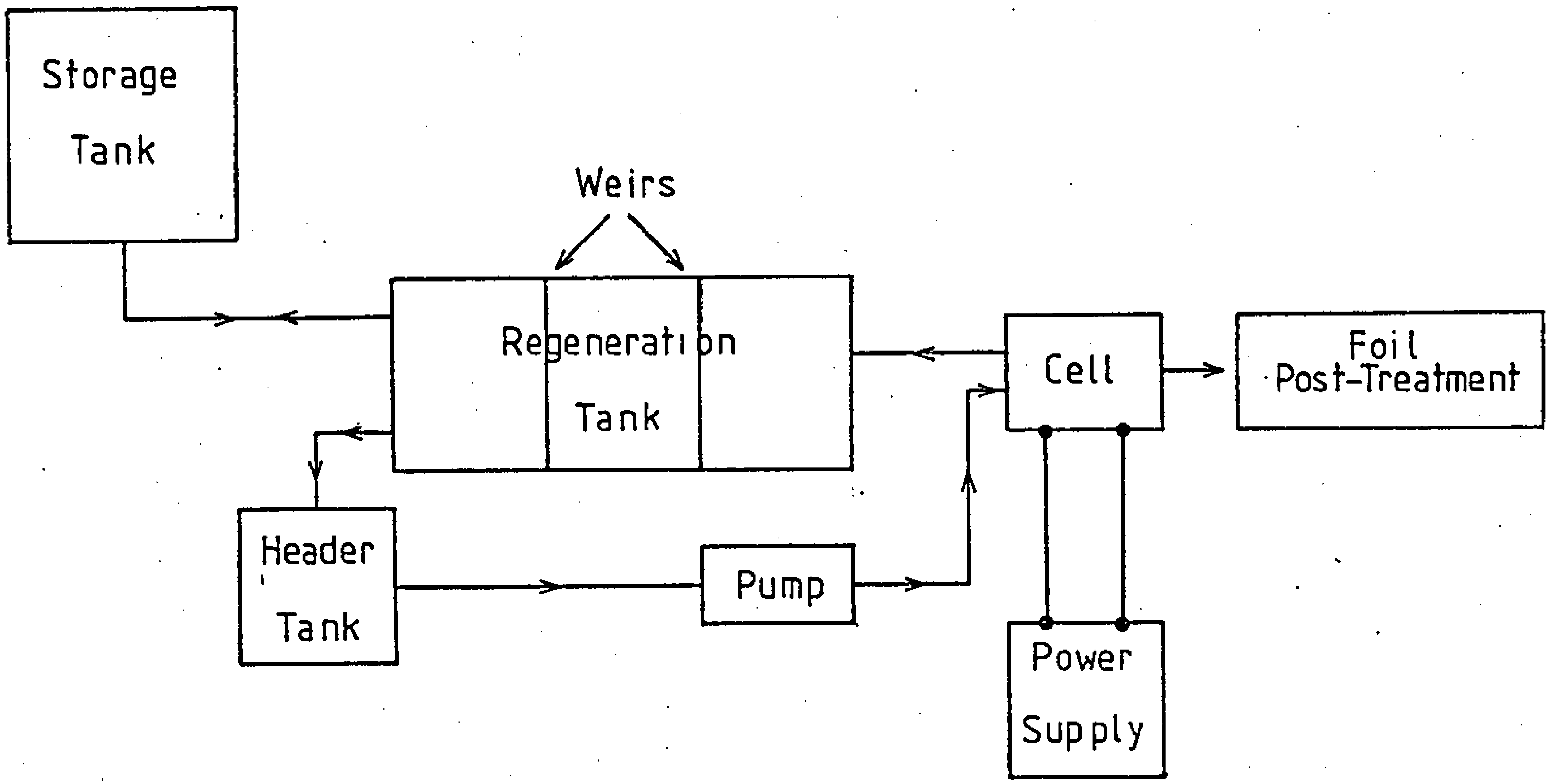


FIG. 4-2. Pilot Plant - Galvanostatic Cathodic Polarization.

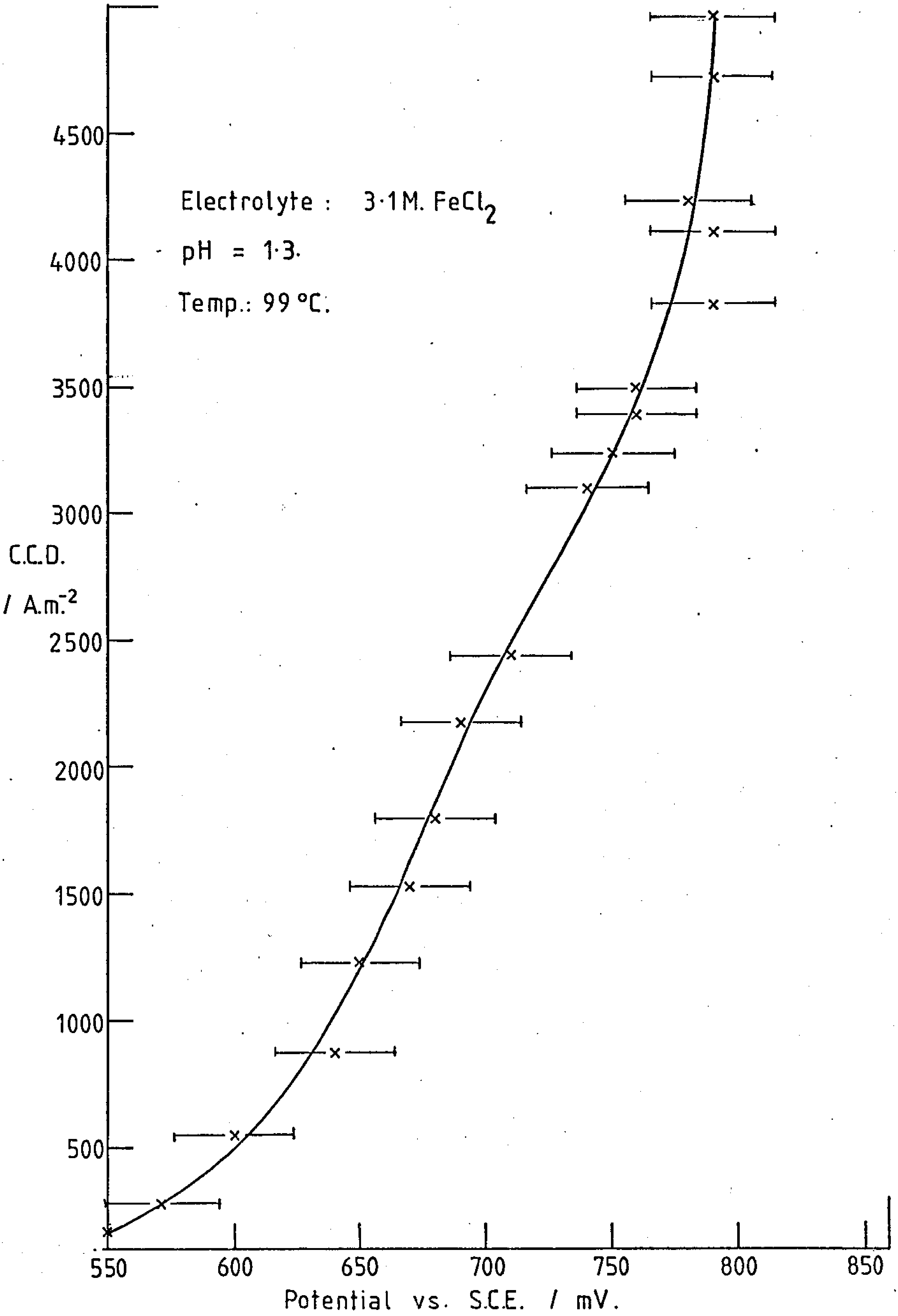


FIG. 4-3. Pilot Plant - Variation of Cell Voltage with Current Density.

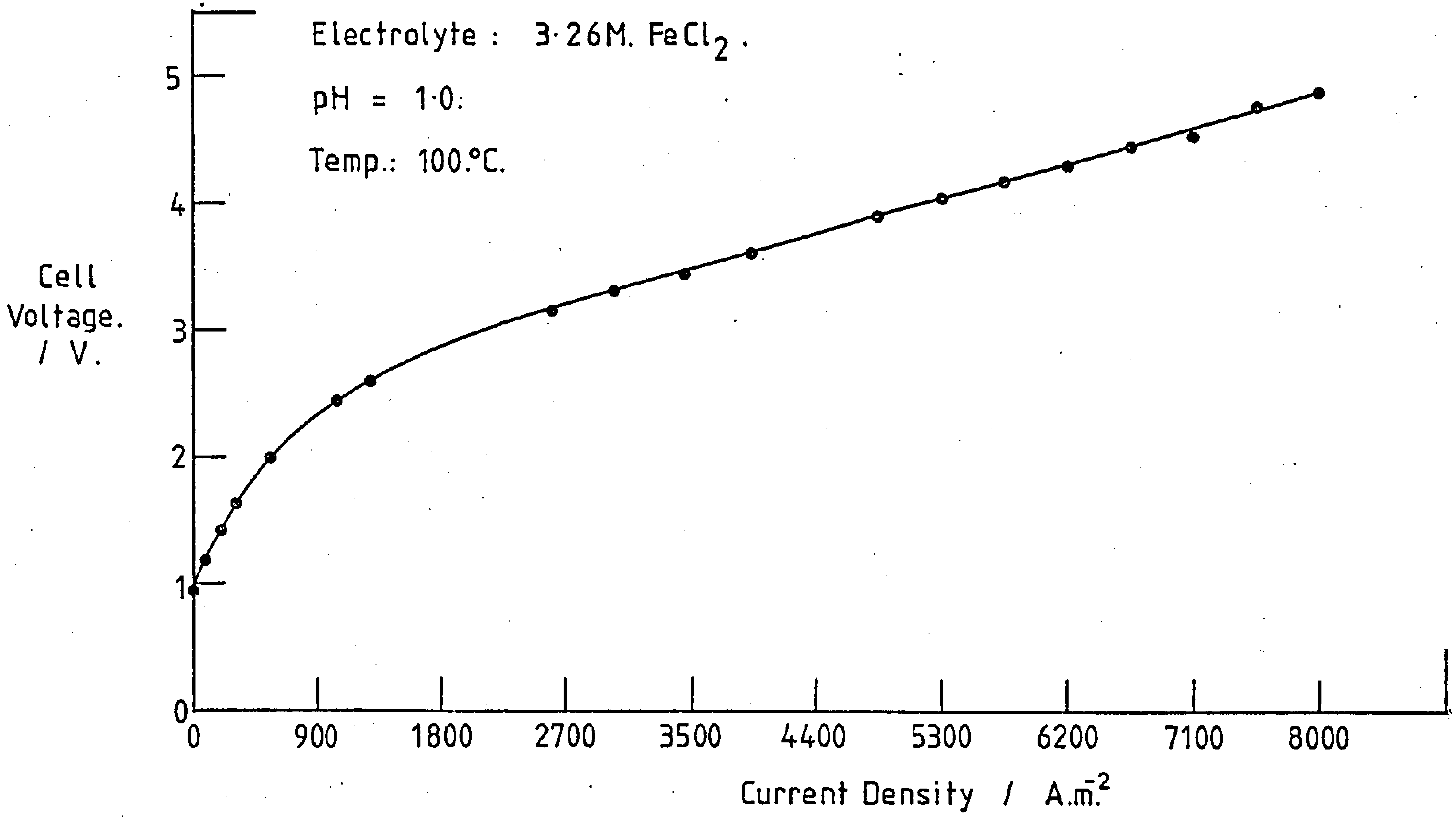


FIG. 4-4. Variation of Electrolyte pH with Time.

Pilot Plant. Run 1.

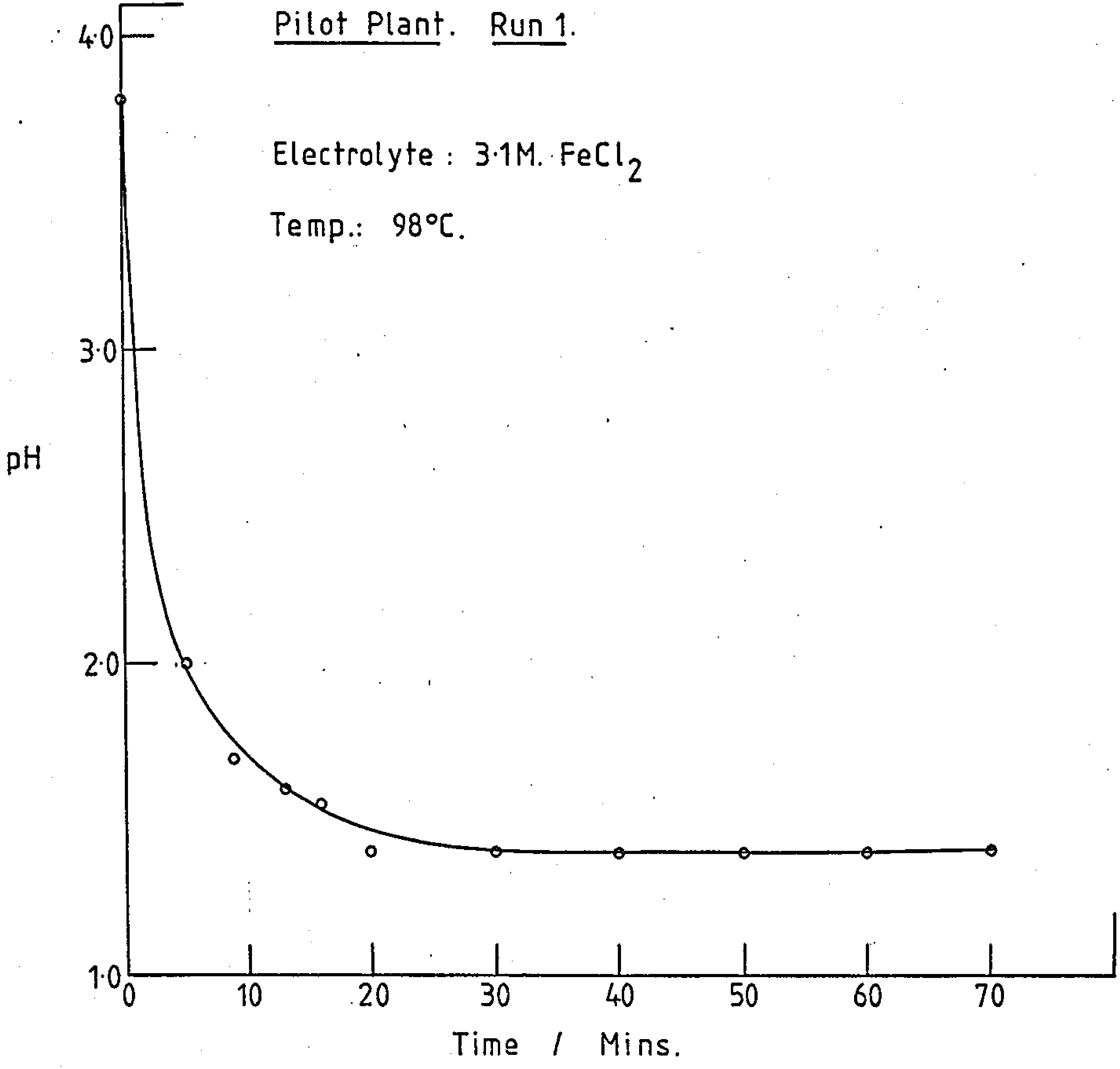


FIG. 4-5. Variation of Electrolyte pH with Time.

Pilot Plant. Run 2.

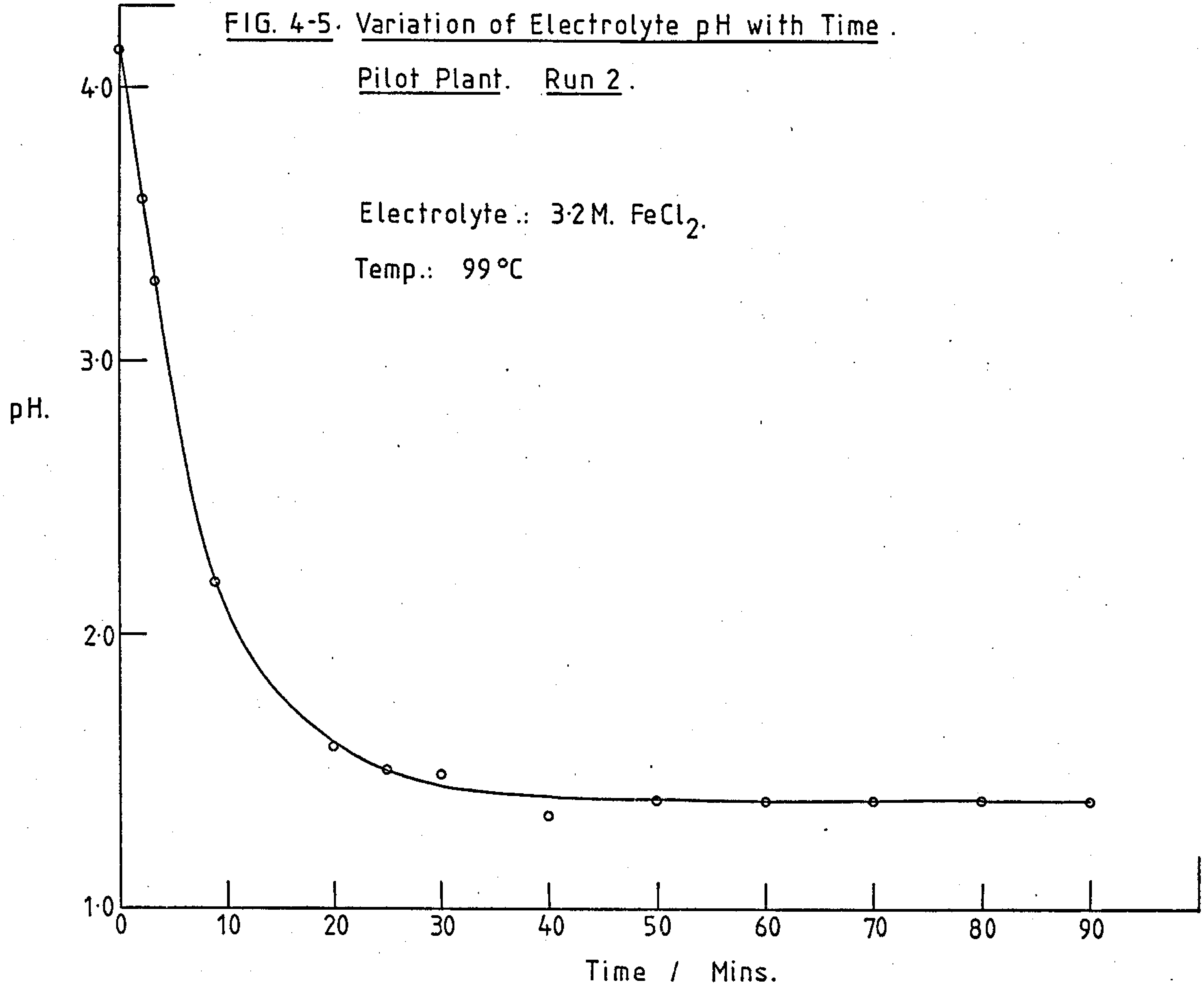
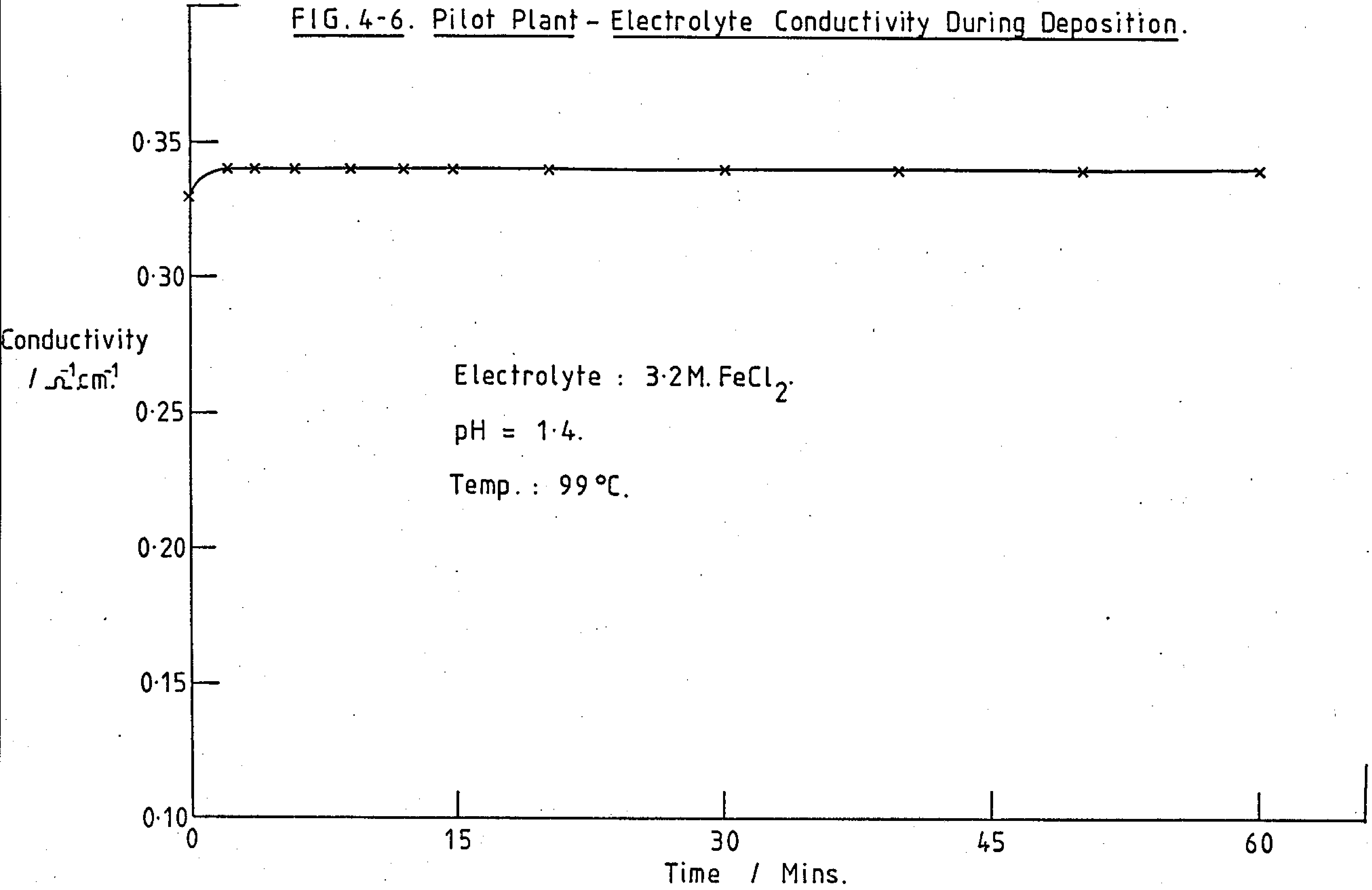


FIG. 4-6. Pilot Plant - Electrolyte Conductivity During Deposition.



Electrolyte : 3·2M. $FeCl_2$.

pH = 1·4.

Temp. : 99 °C.

FIG. 5-1. Conductivity Cell. — Philips Model PW 9517. (Immersion.)

Cell Constant : 28·3 cm^{-1}.

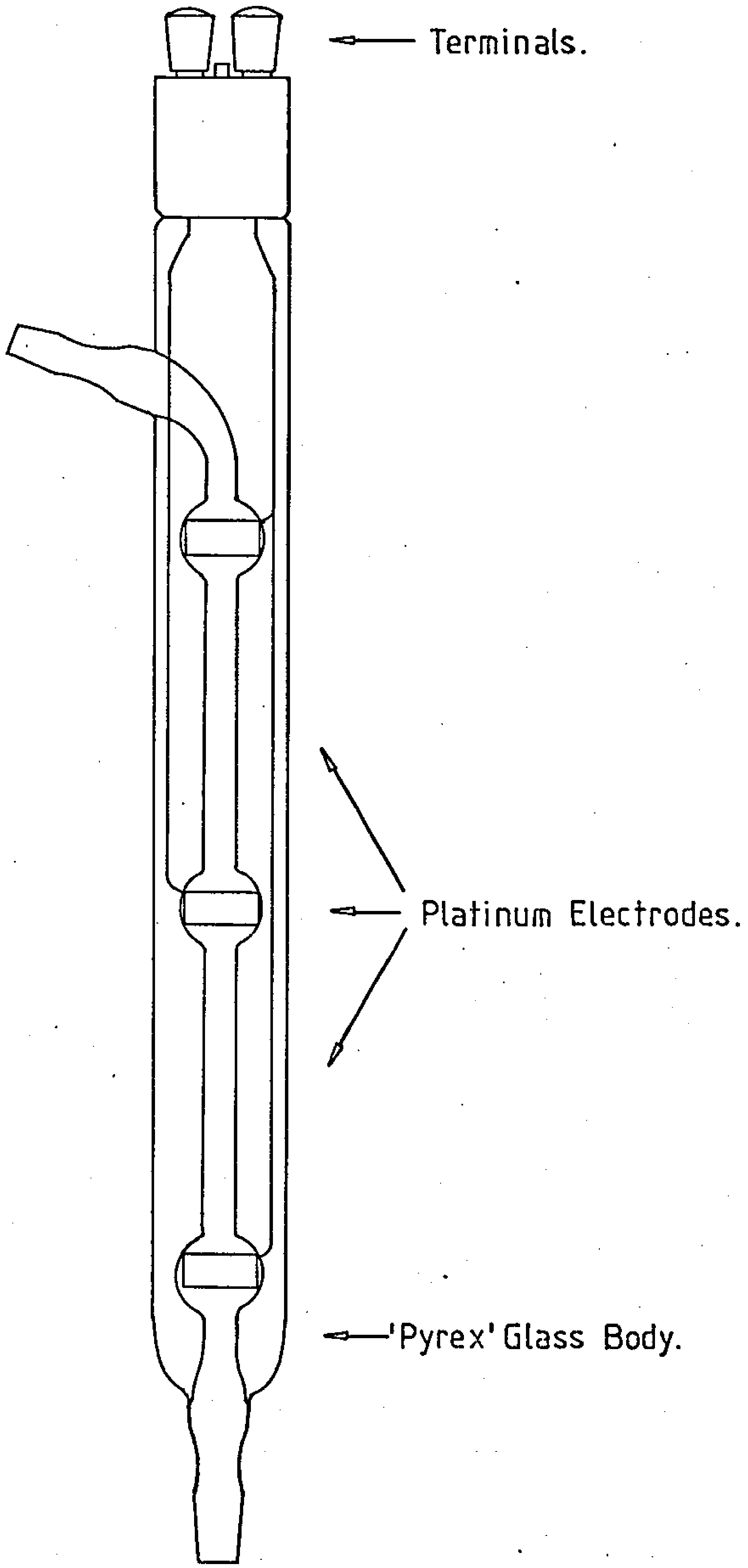
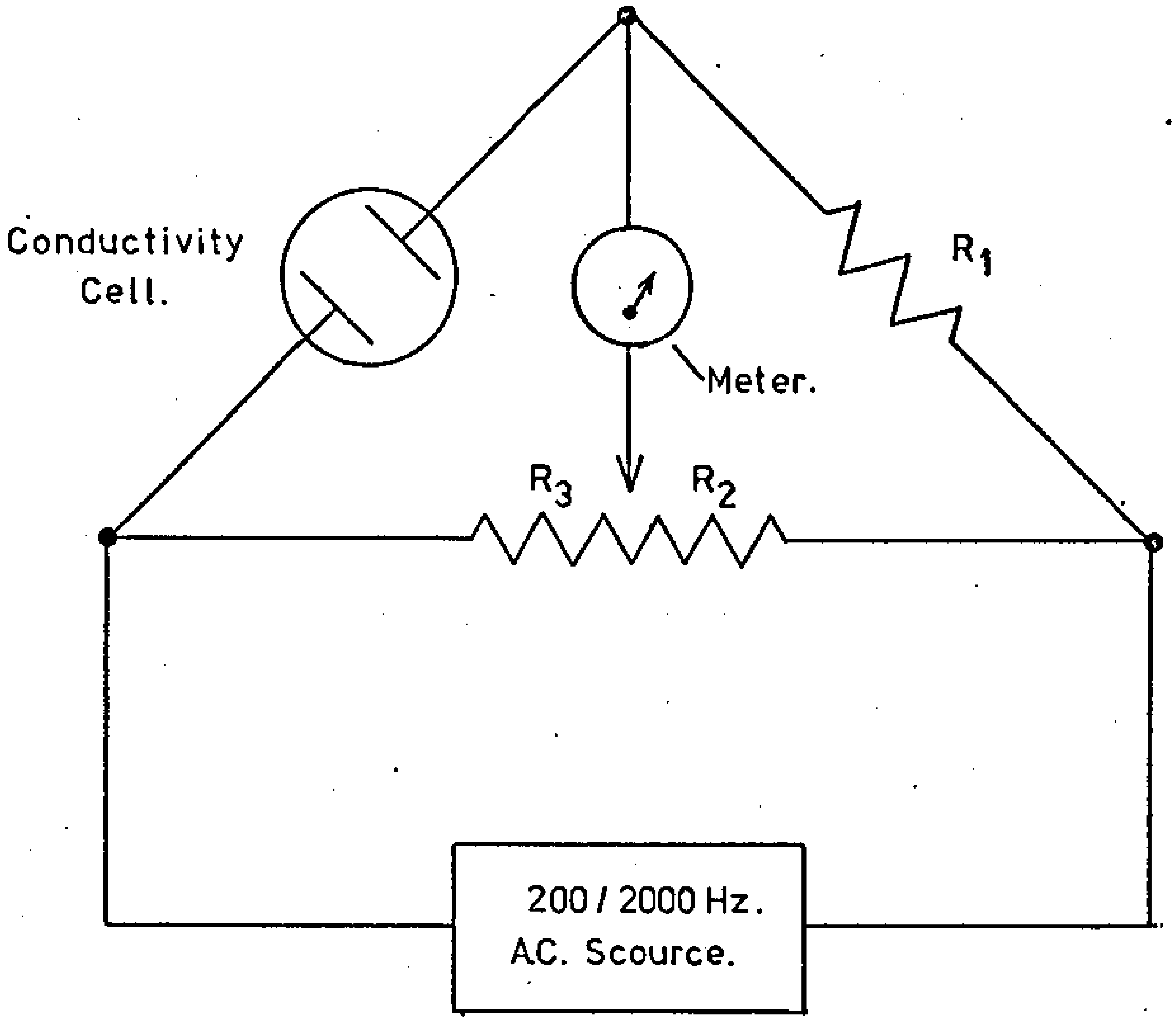


FIG. 5-2. Schematic Representation of Conductivity Meter.



At Balance: $R_1 / R_2 = \text{Cell } R / R_3$

FIG. 5-3a. Planar Cathode.

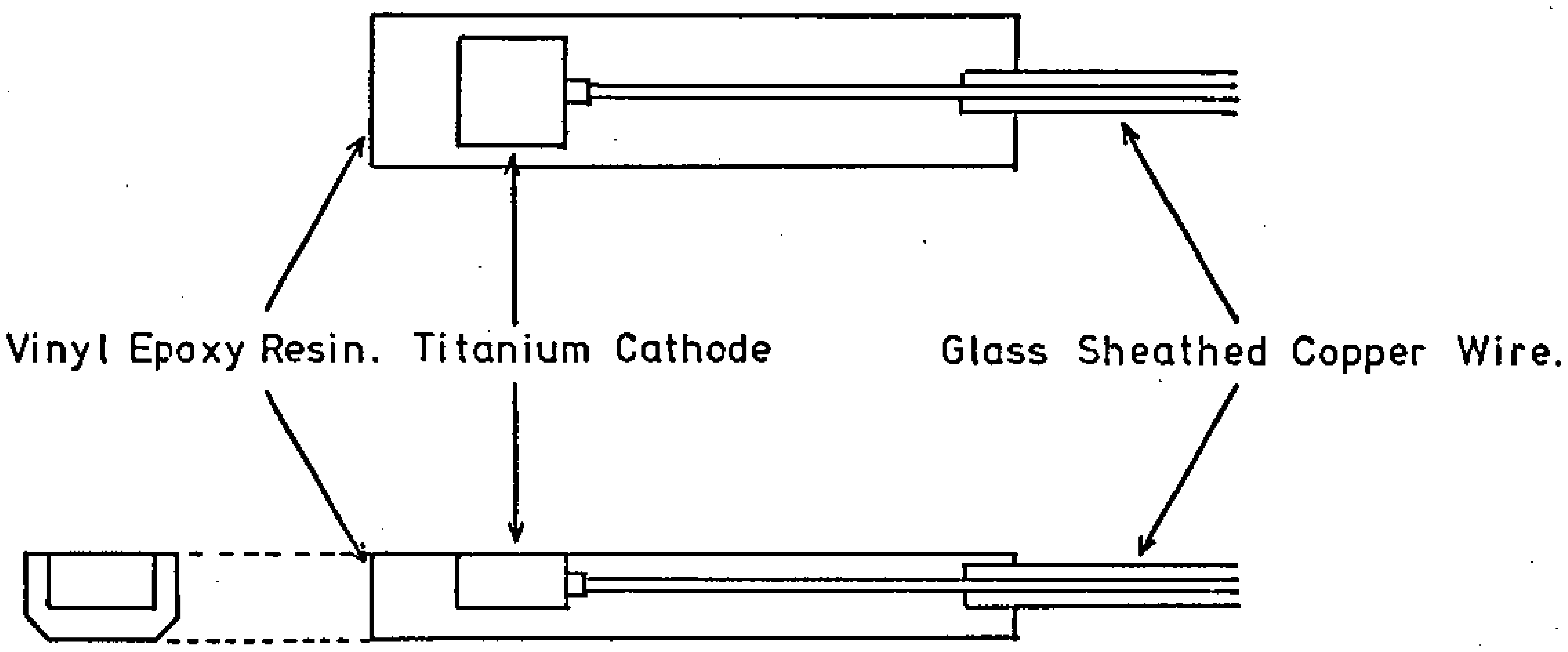


FIG. 5-3b Planar Graphite Anode.

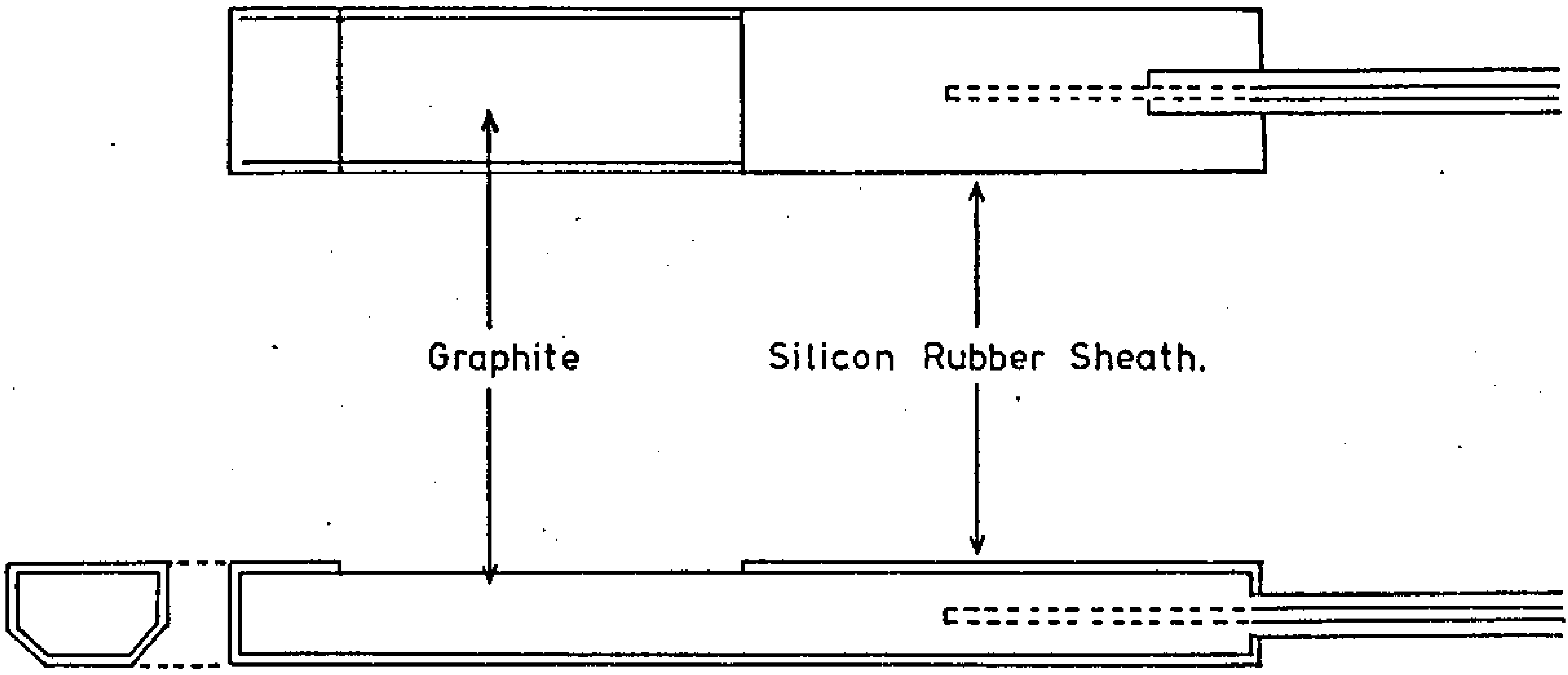


FIG. 5-4. Reaction Cell Used for Initial Polarization Work.

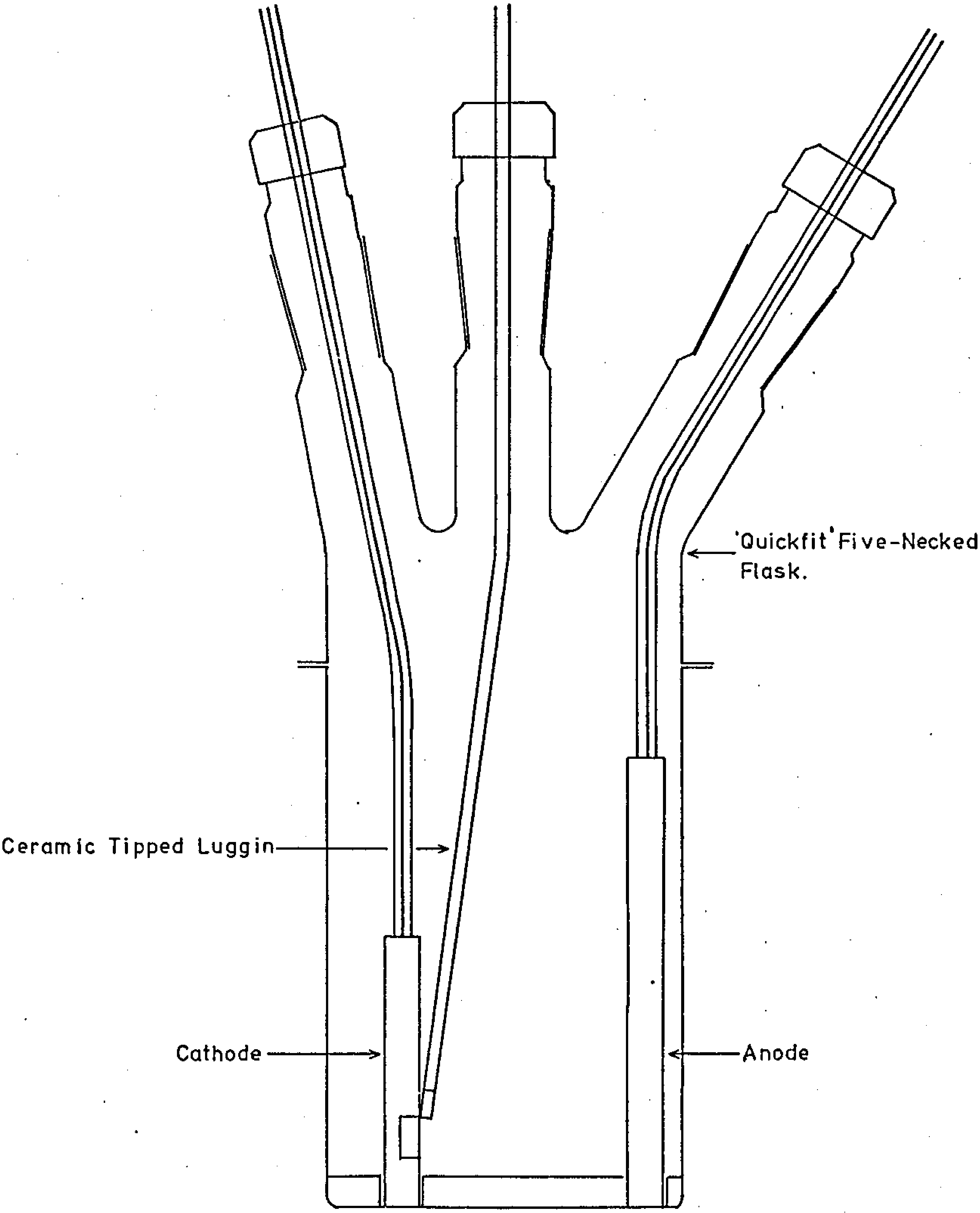
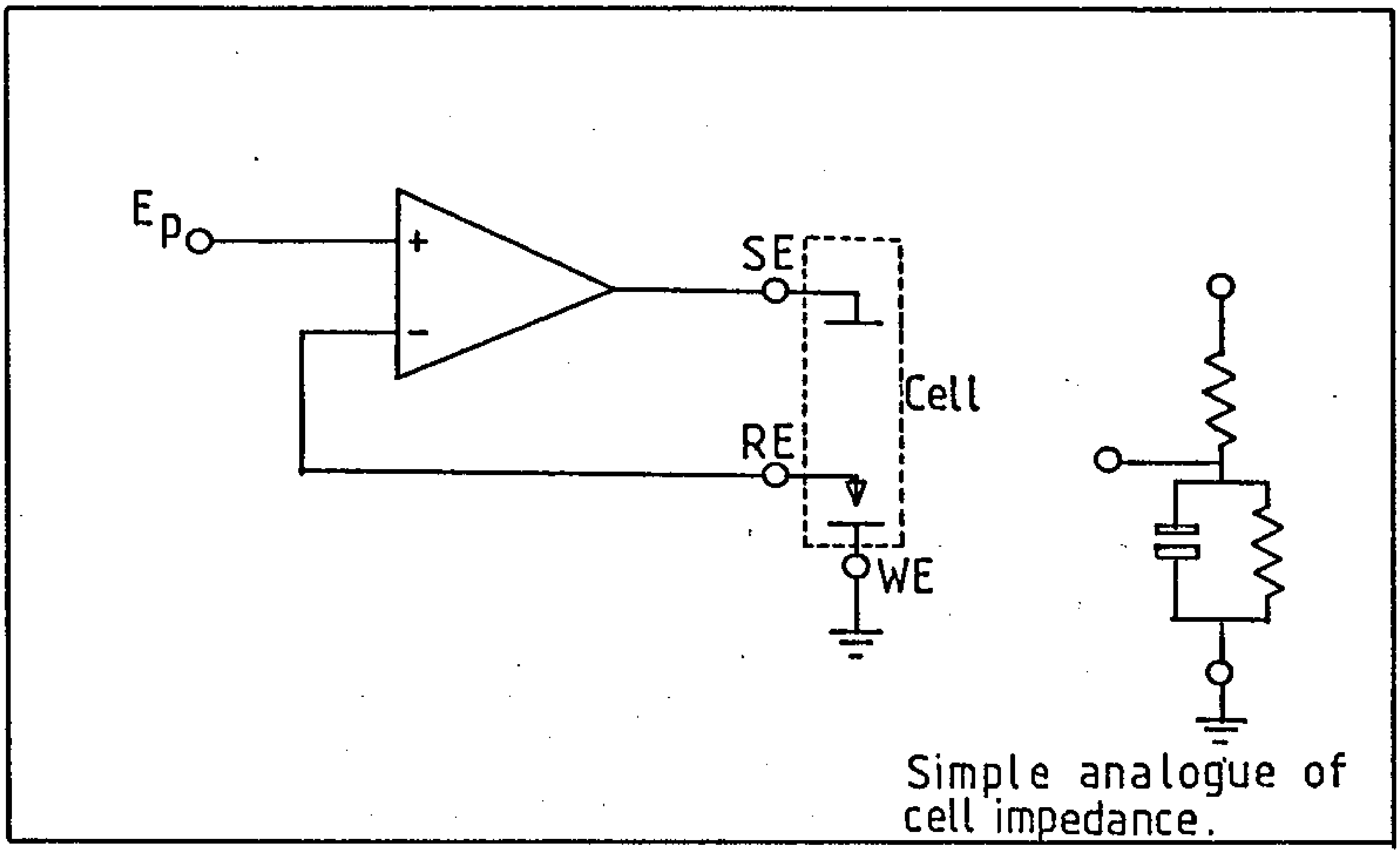


FIG. 5-5a. Basic Potentiostat Circuit.



Simple analogue of cell impedance.

FIG. 5-5b. Practical Potentiostat Circuit.

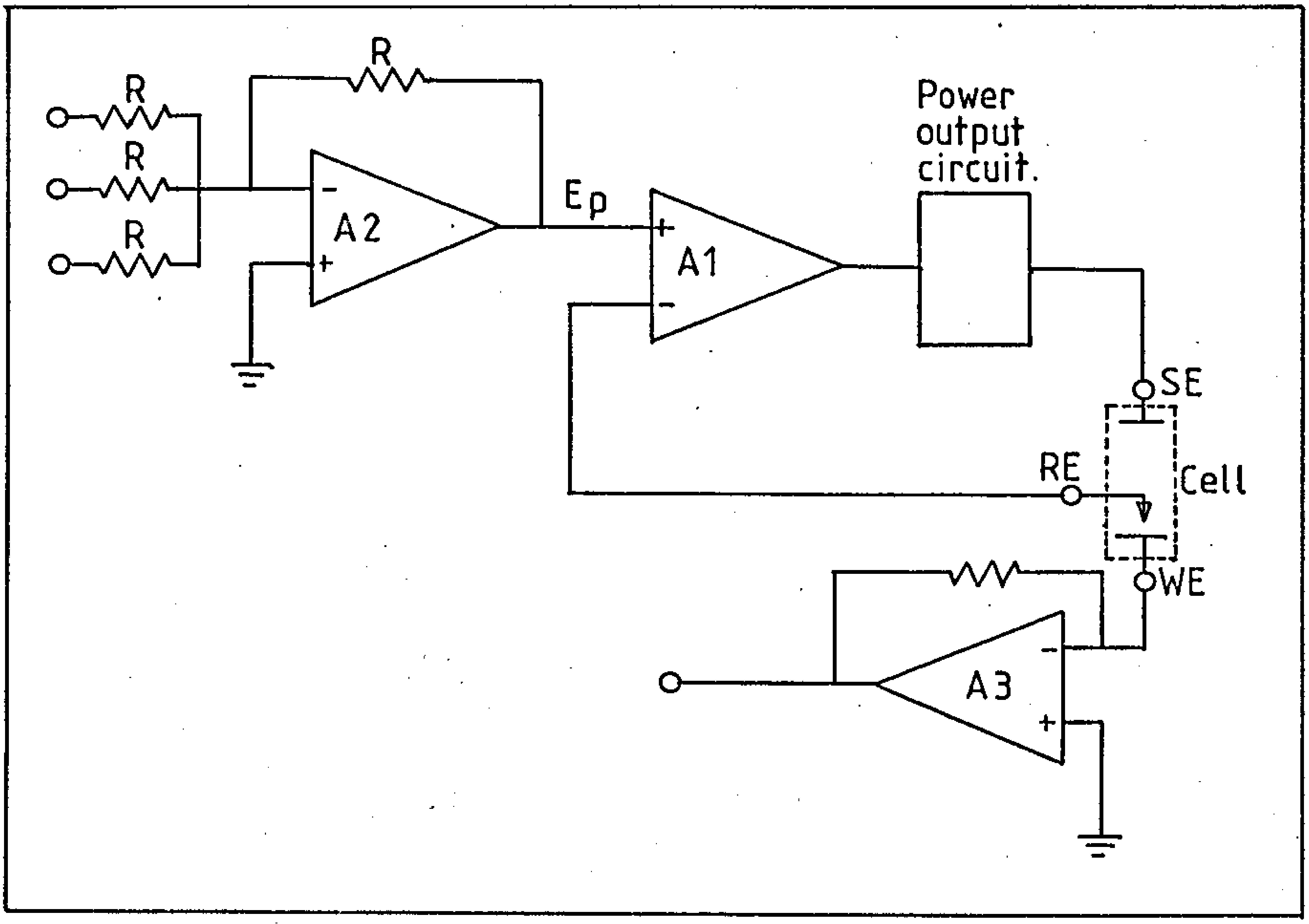


FIG. 5-6. Electrolytic Cell with Rotating Cylinder Electrode.

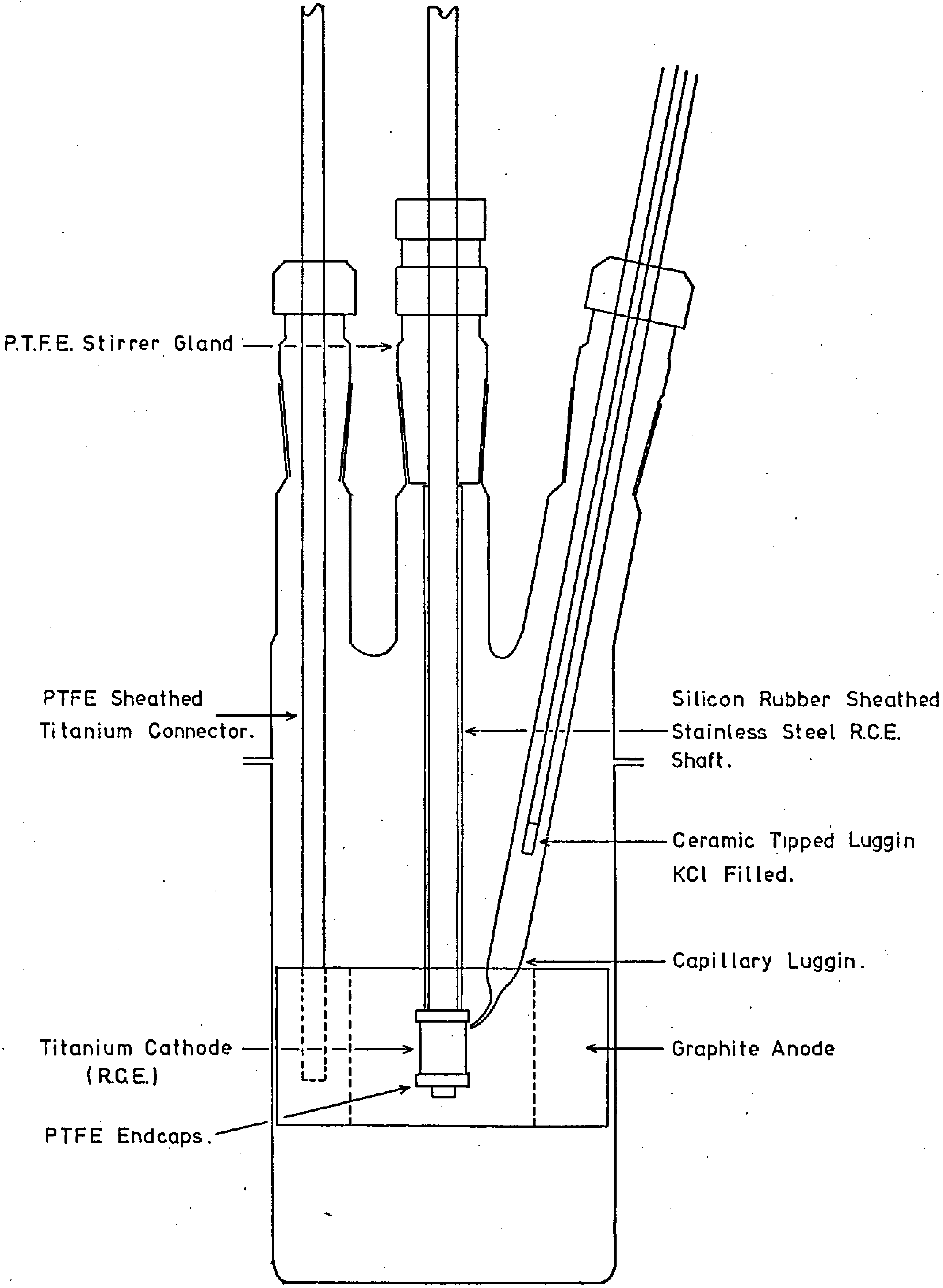


FIG. 6-1. Conductivity vs. Temperature, Ferrous Chloride only.

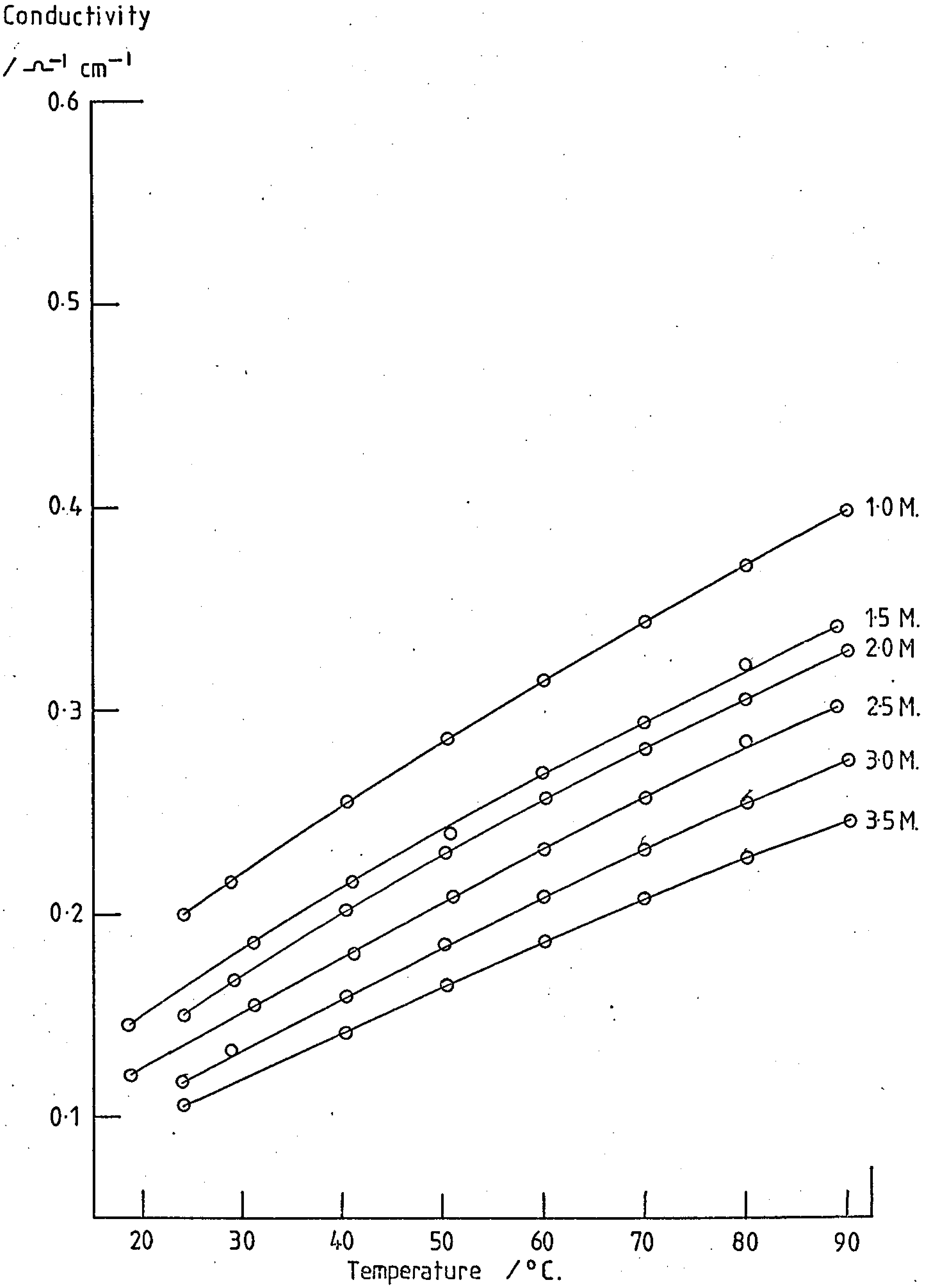


FIG. 6-2. Conductivity vs. Temperature, Ferrous Chloride (1·5 M.) and Calcium Chloride (1·0 - 2·4 M.)

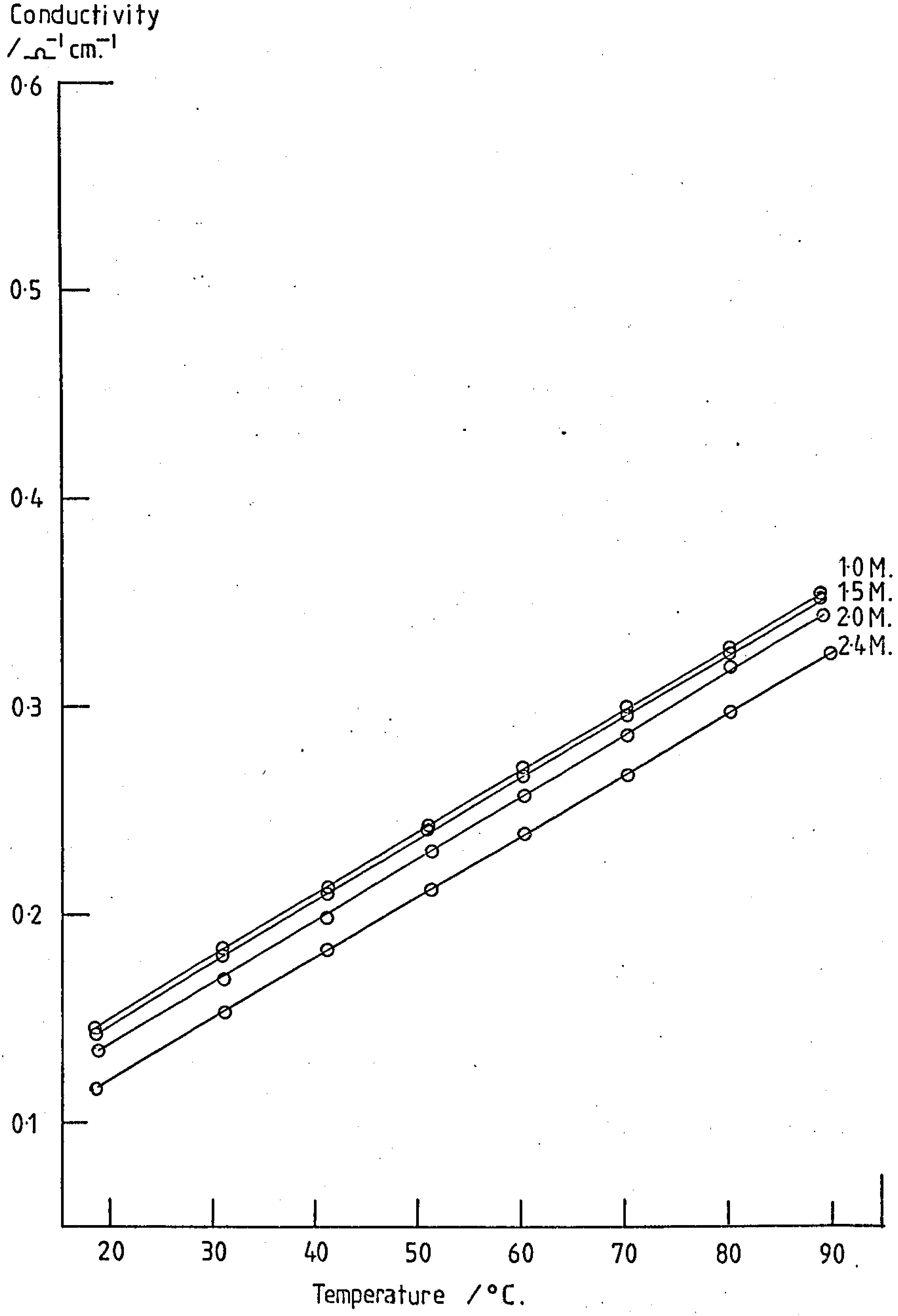


FIG. 6-3. Conductivity vs. Temperature, Ferrous Chloride (1·5M.) and Magnesium Chloride (1·8–5·6M.)

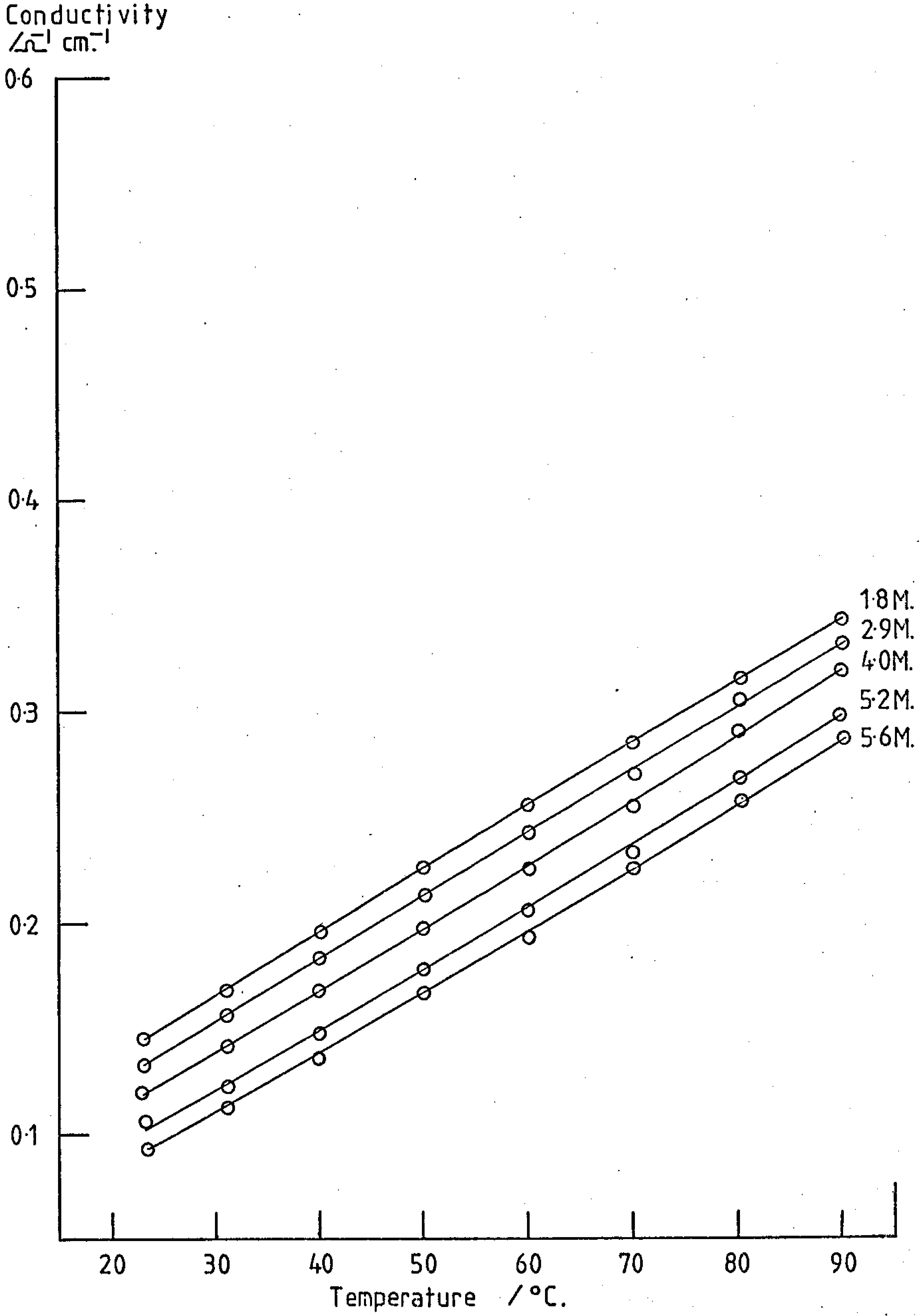


FIG. 6-4. Conductivity vs. Temperature.

Ferrous Chloride (1·5 M.) and Sodium Chloride (0·5–2·75 M.)

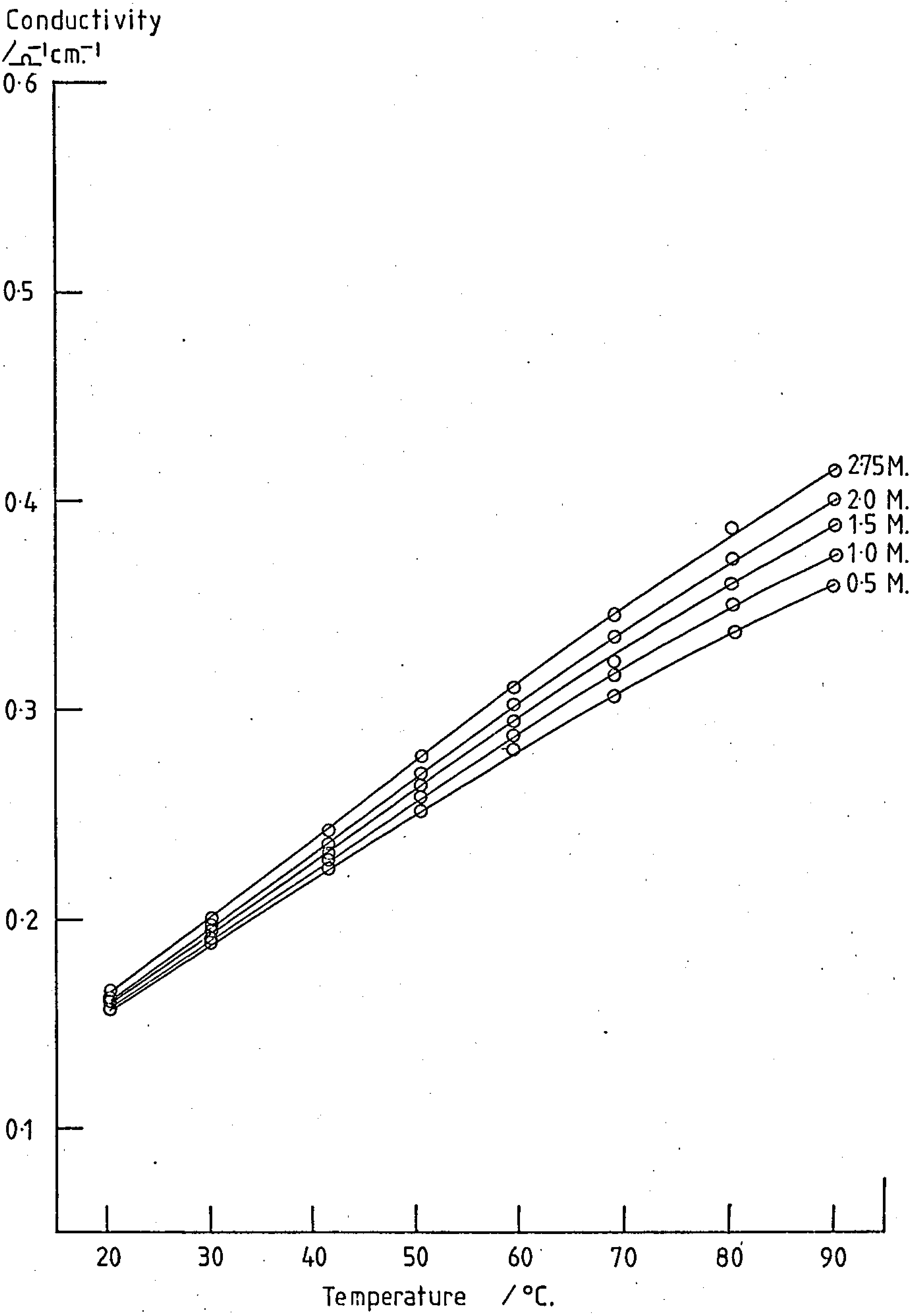


FIG. 6-5. Conductivity vs. Temperature, Ferrous Chloride (1·5M.) and Ammonium Chloride (0·75–3·0M.)

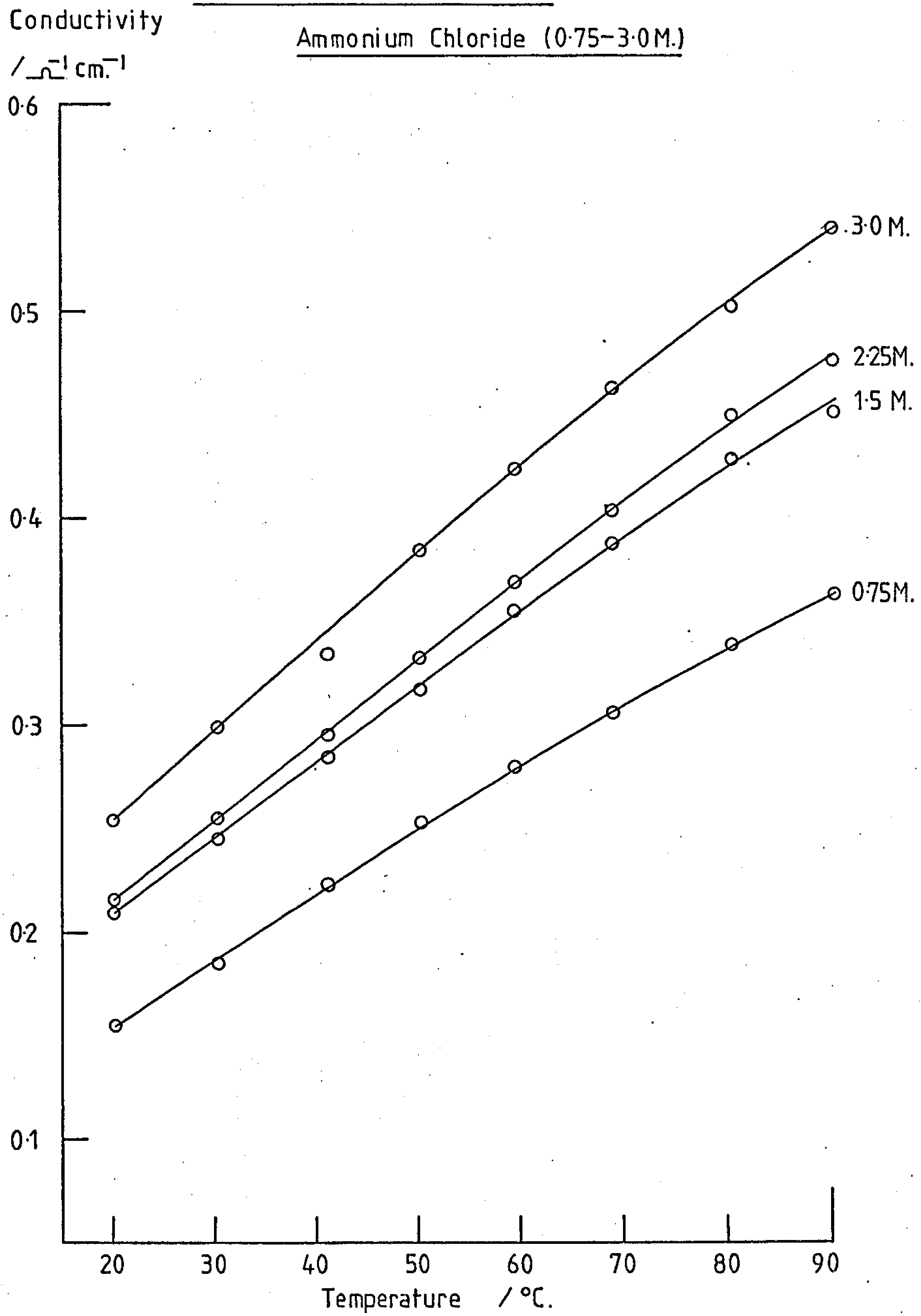


FIG. 6-6. Conductivity vs. Temperature,

Ferrous Chloride (1·5 M.) and Potassium Chloride (0·4–2·1 M.)

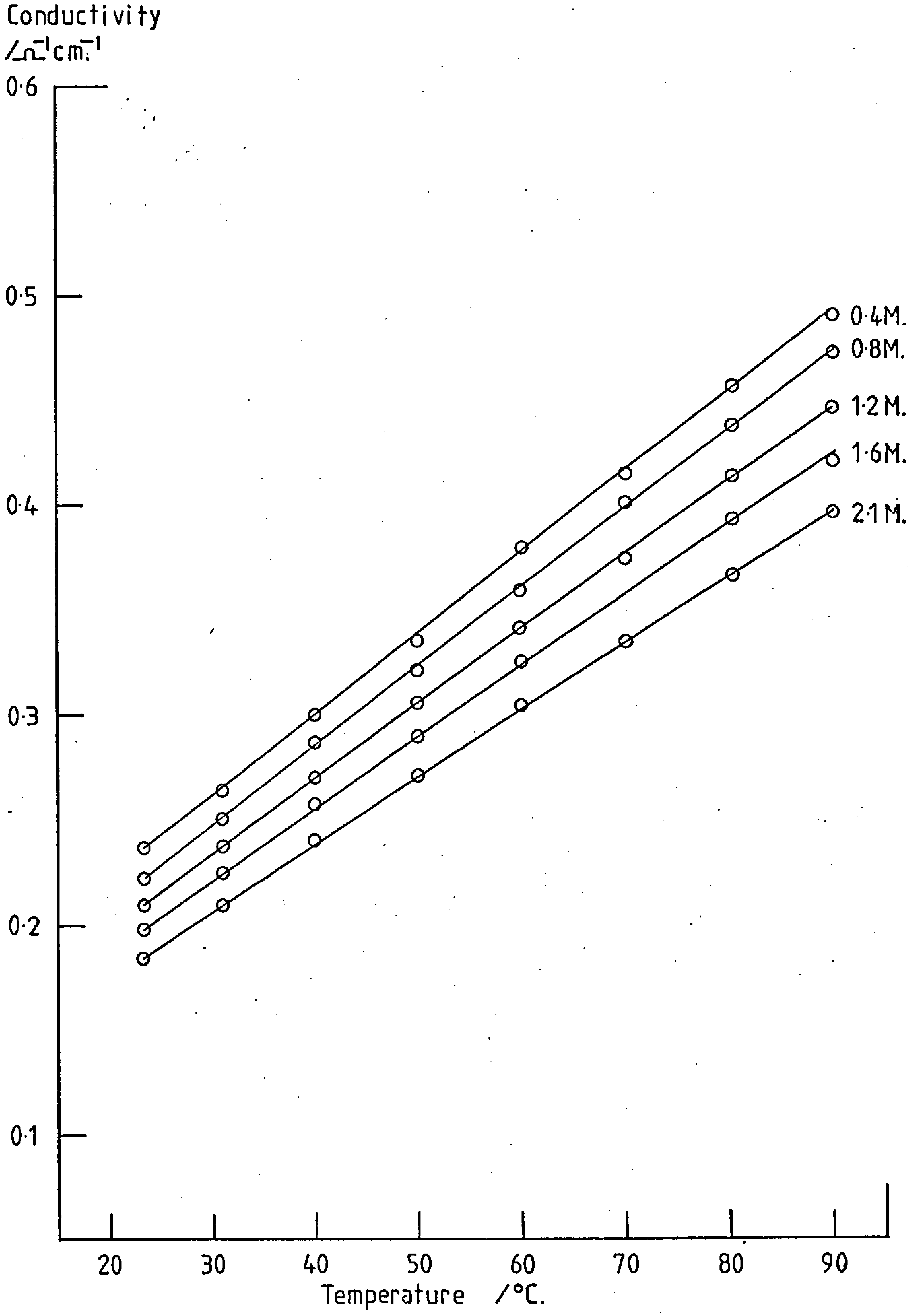


FIG. 6-7. Plot of Conductivity vs. [$FeCl_2$].

pH = 0·0.

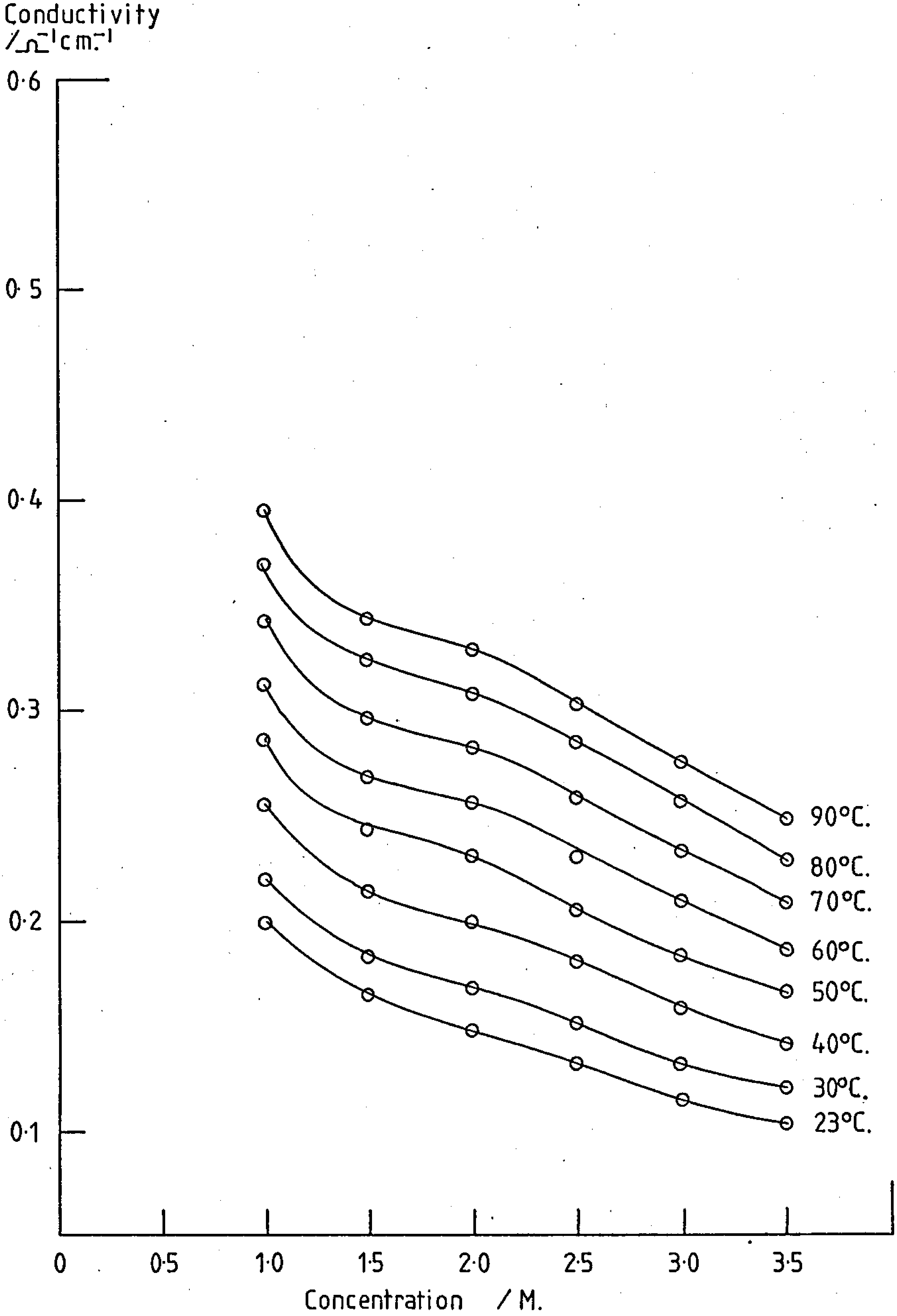


FIG. 6-8. Plot of Conductivity vs. [$CaCl_2$] in 1·5M. $FeCl_2$.
pH = 0·0.

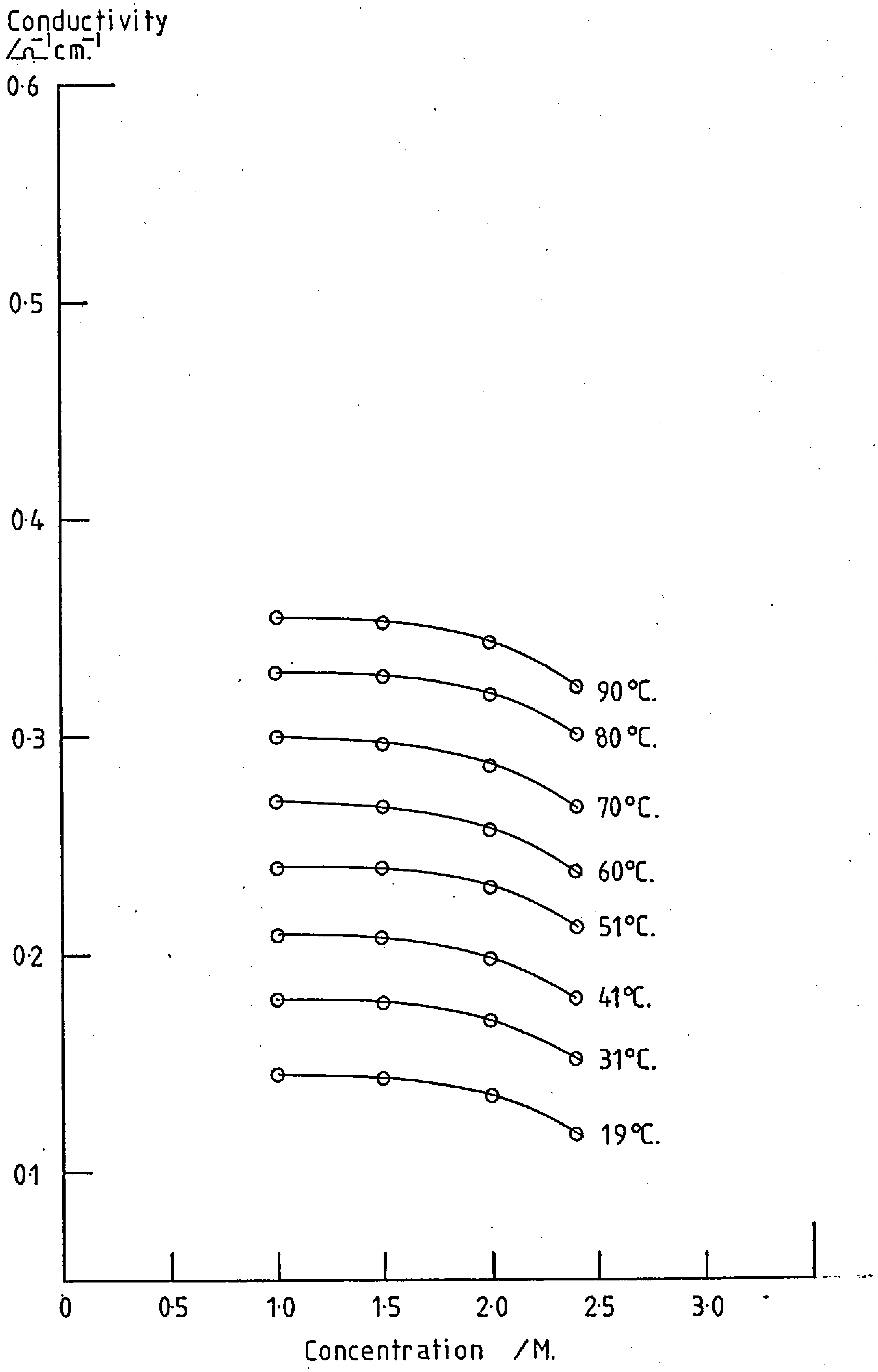


FIG. 6-9. Plot of Conductivity vs. [$MgCl_2$] in 1·5M. $FeCl_2$.

pH = 0·0.

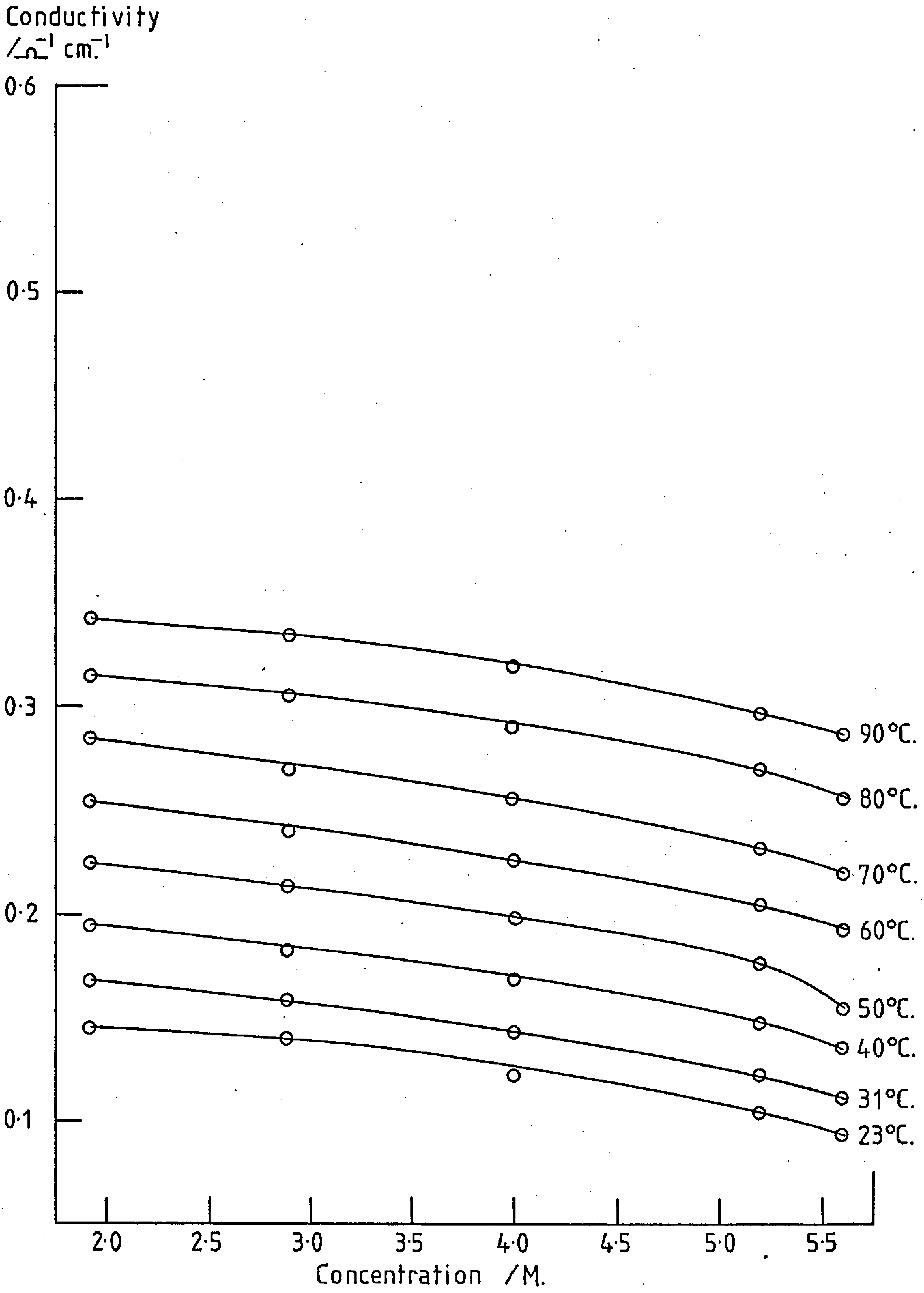


FIG. 6-10. Plot of Conductivity vs. [NaCl] in 1·5 M. $FeCl_2$. pH = 0·0.

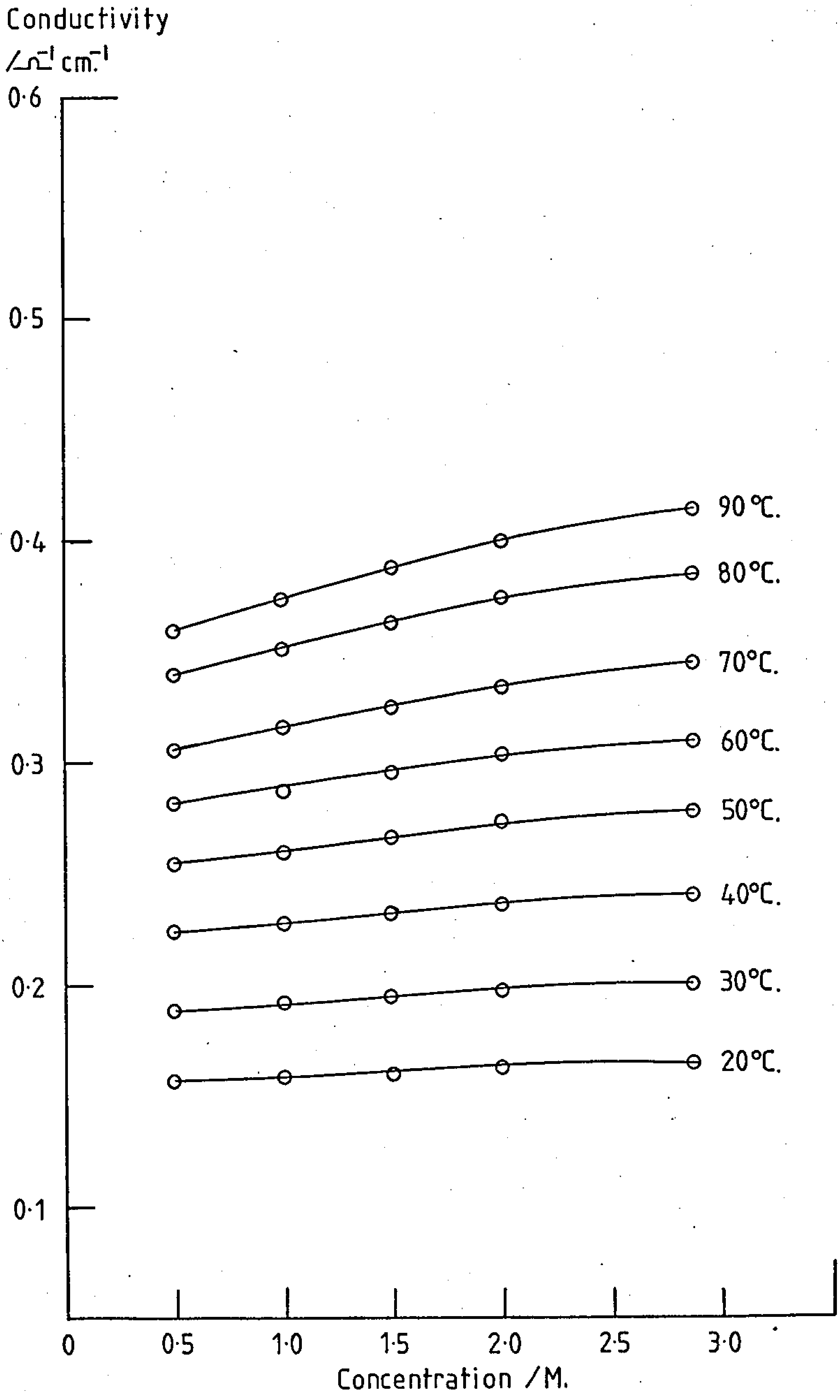


FIG. 6-11. Plot of Conductivity vs. [NH_4Cl] in 1·5M. $FeCl_2$. pH = 0·0.

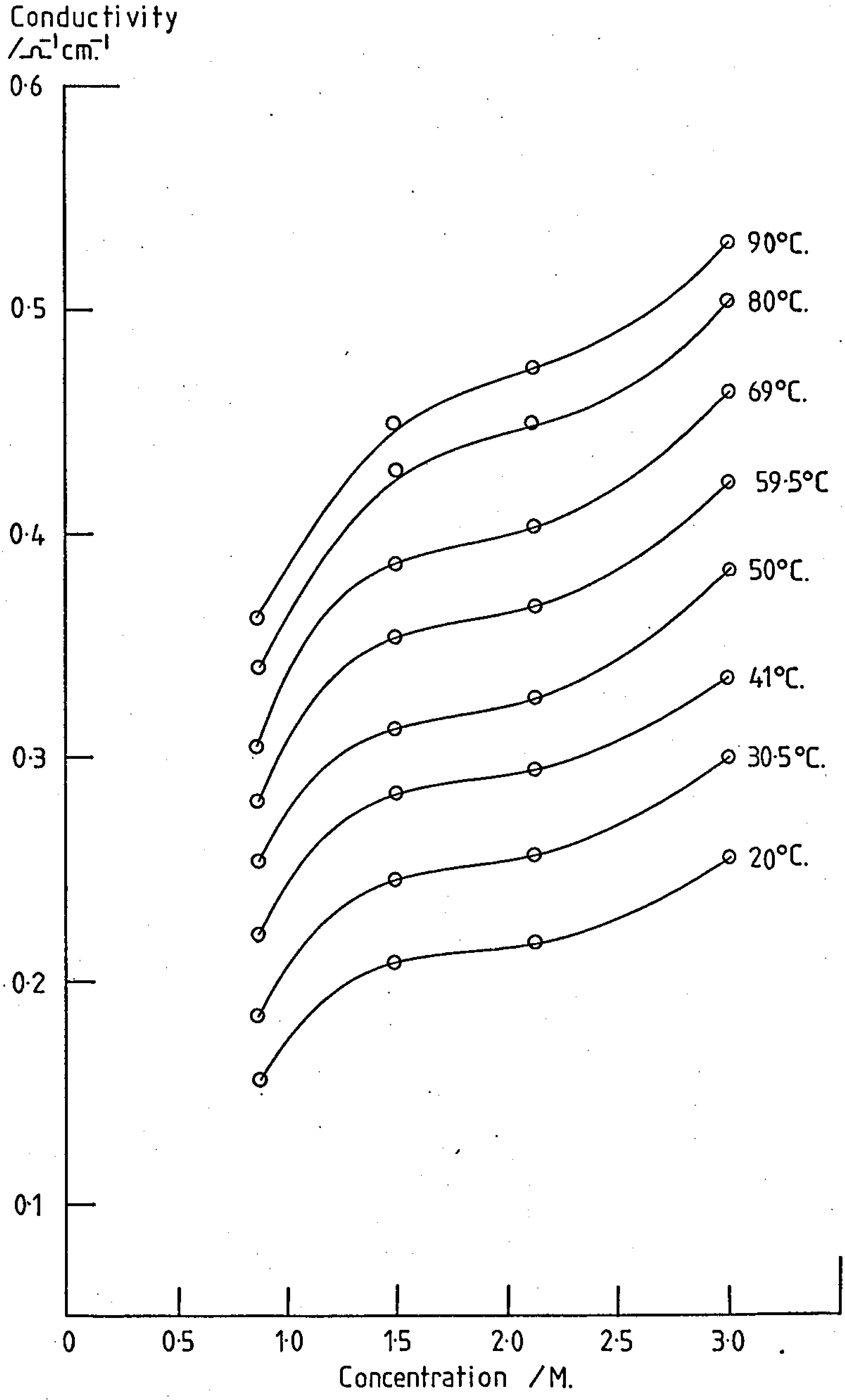


FIG. 6-12. Plot of Conductivity vs. [KCl] in 1·5M. $FeCl_2$. pH = 0·0.

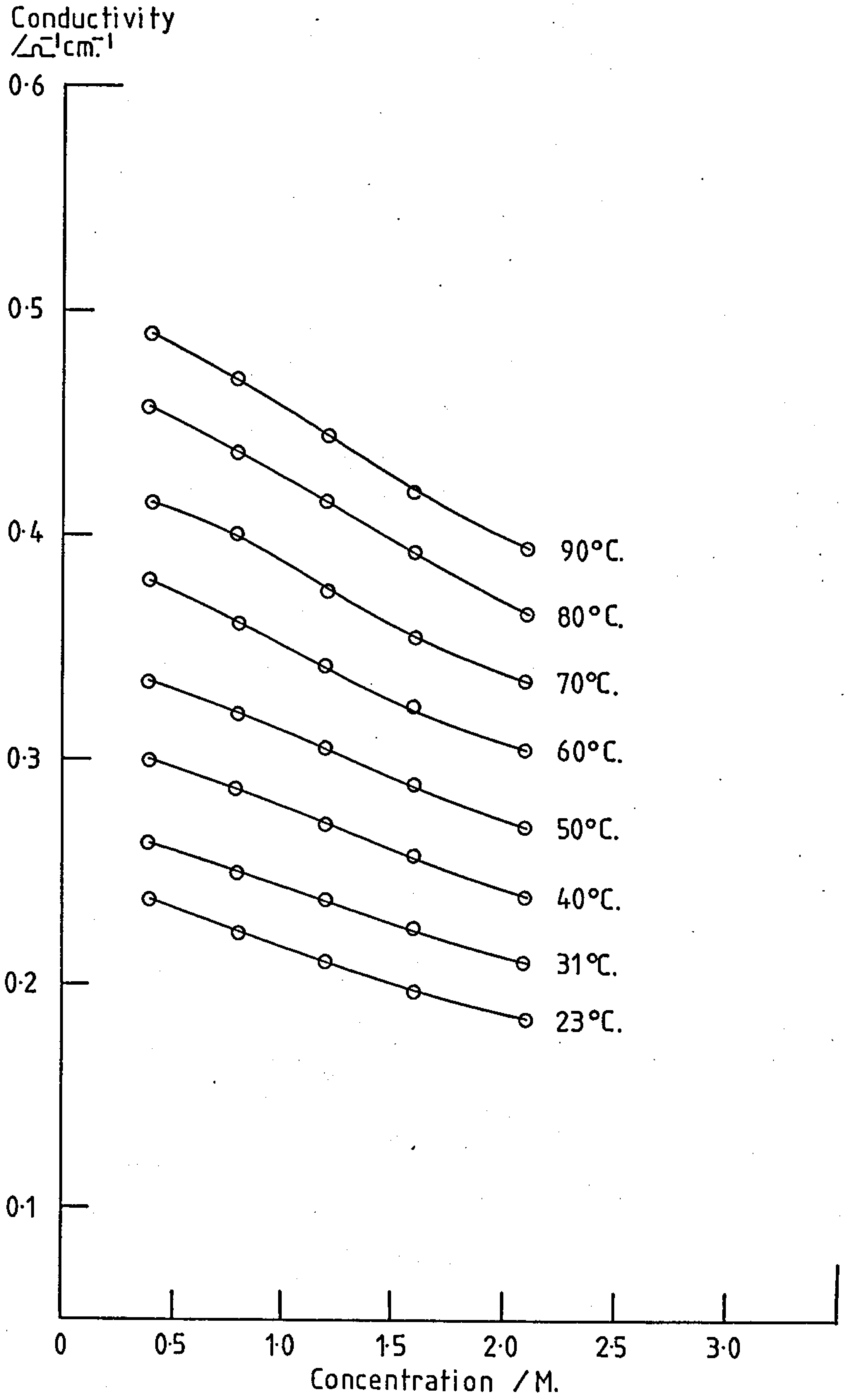


FIG.6-13. Plot of Conductivity vs. pH.

3·5 M. Ferrous Chloride, Temperature = 90·0°C.

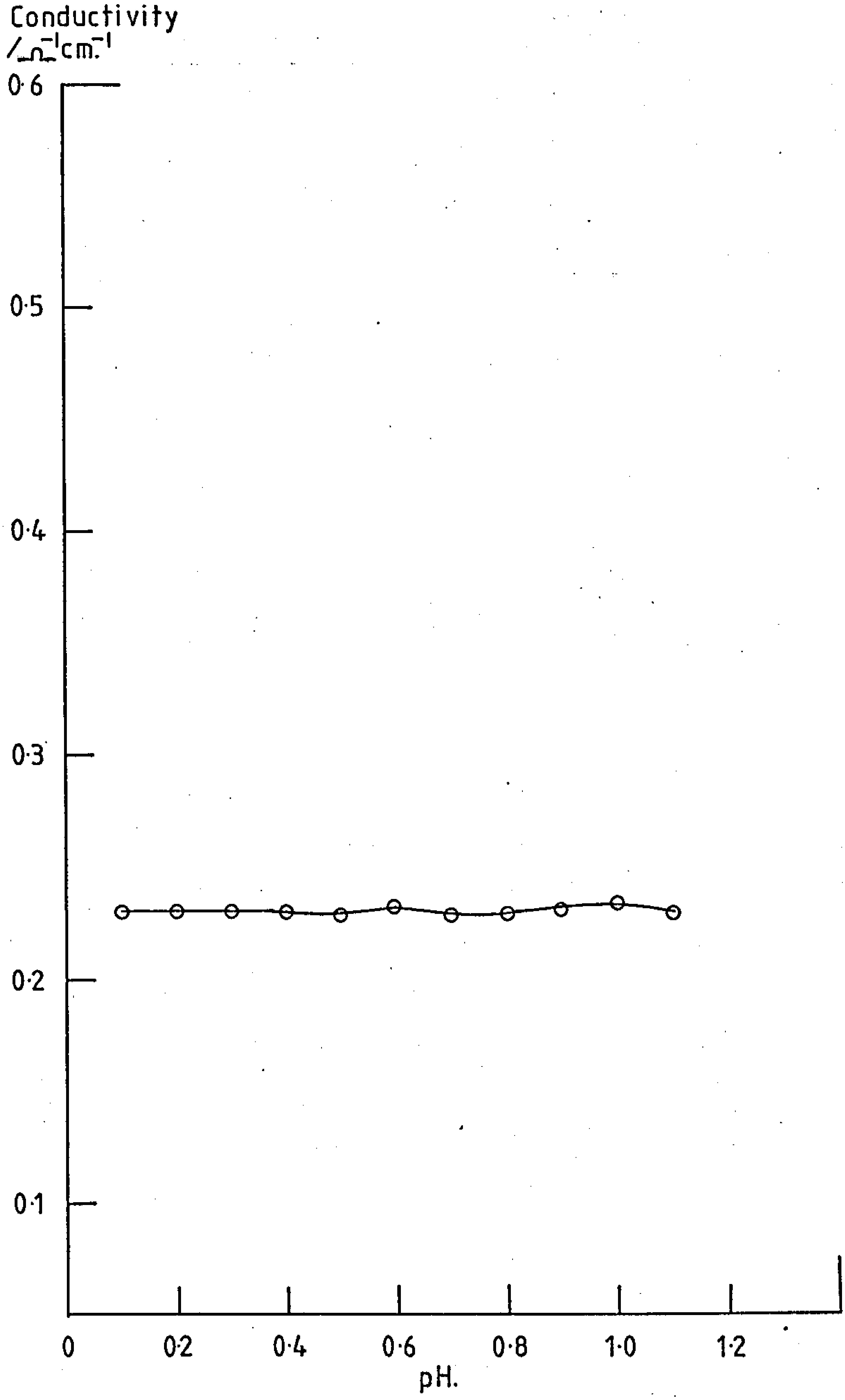


FIG. 6-14. Summary of Conductivity vs. Temperature Results.

All Electrolytes - 1·5M. $FeCl_2$. and 1·5M. Salt.

pH = 0·0.

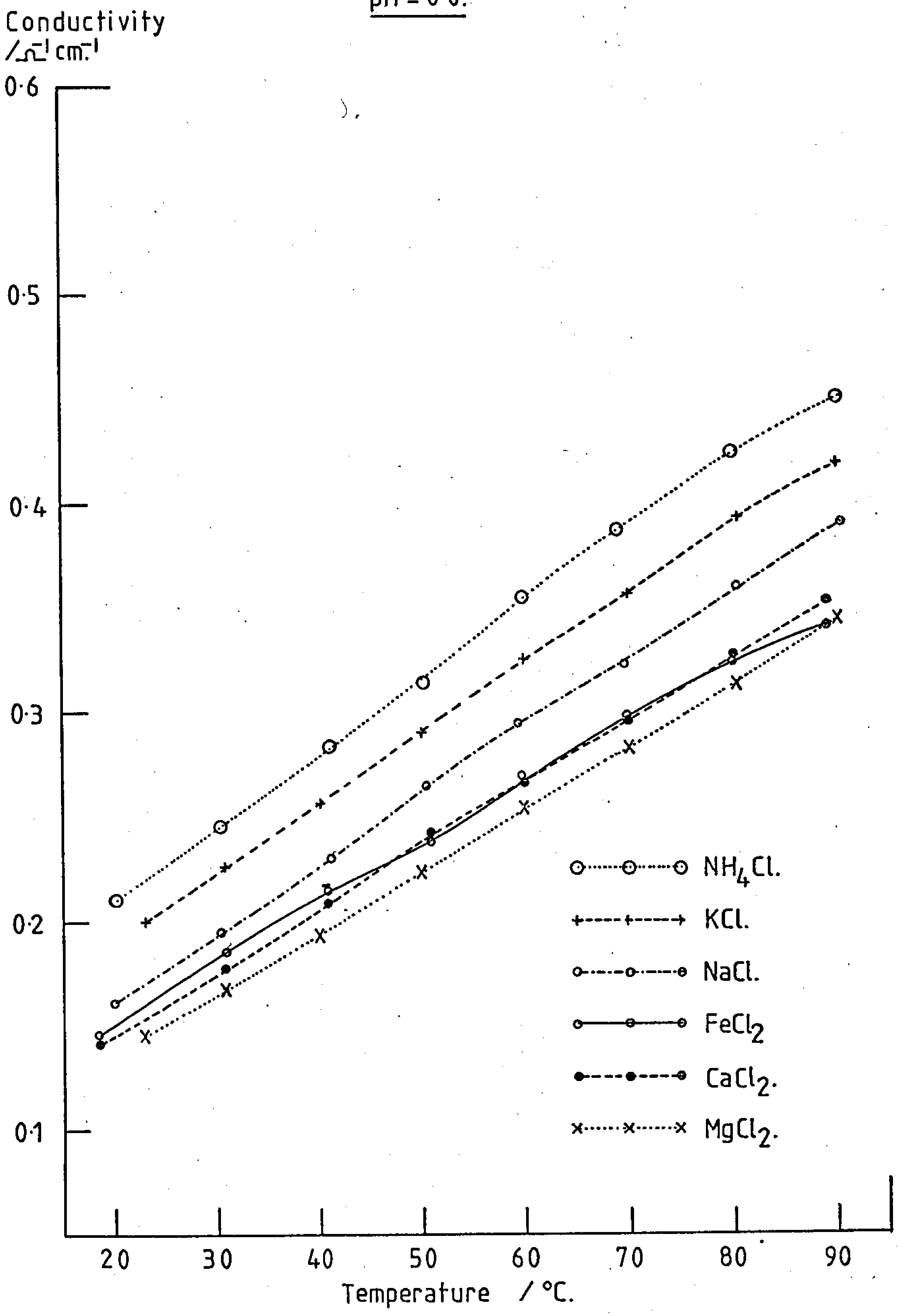


FIG. 6-15. Summary of Conductivity vs. 'Conductivity Salt' Concentration. (Temp. = 90°C., pH = 0·0.)

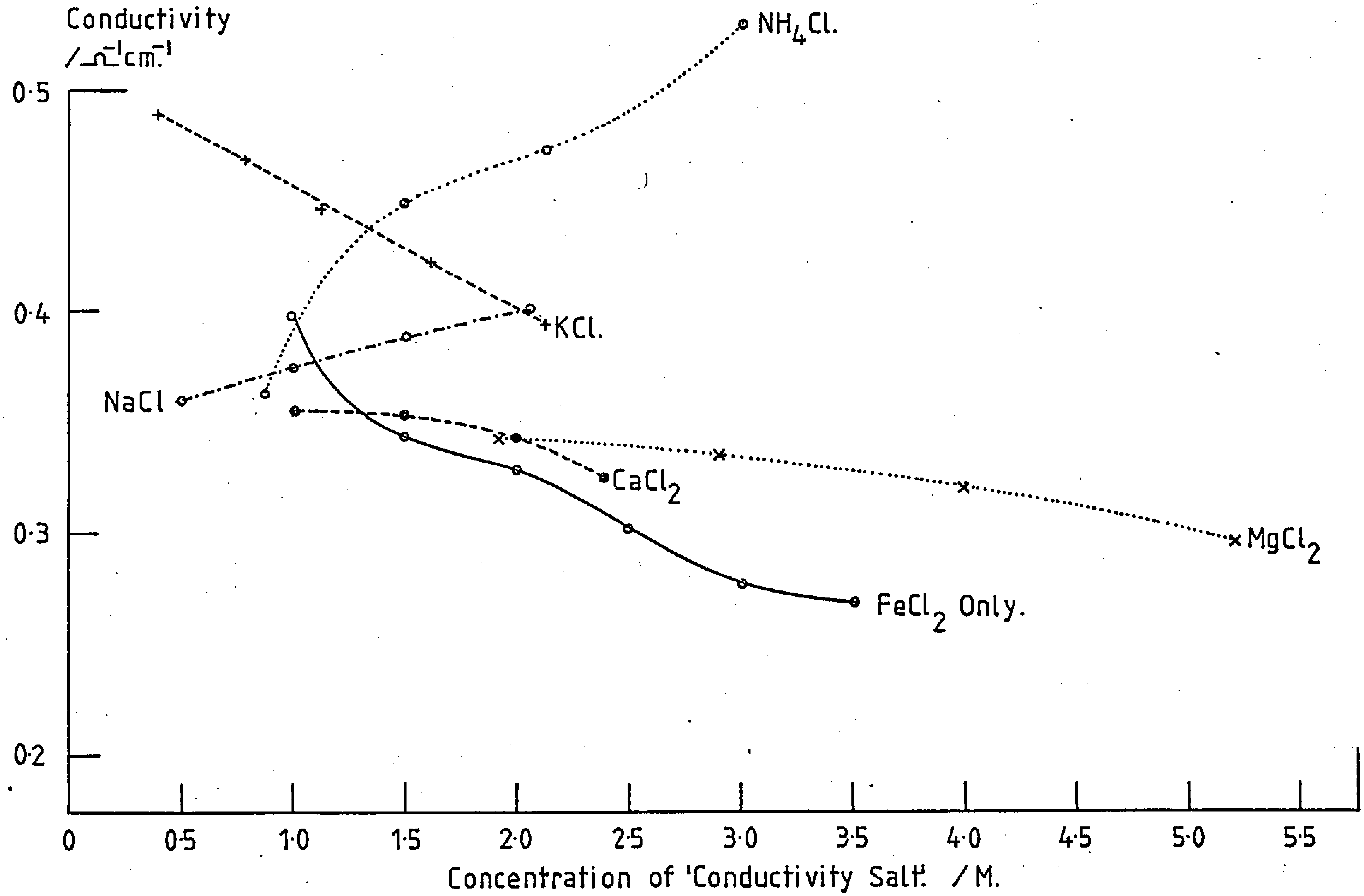


FIG. 6-16. Arrhenius Plot of Conductivity / Temperature Data.

Concentration of Salts = 2·0 M.

pH = 0·0.

FIG. 6-17. Cathodic Polarization - Effect of Cracking of the Deposit.

Electrolyte : 3·5M $FeCl_2$.

pH = 0·5

Temp.: 18 °C.

FIG. 6-18. 'Electrochemical Noise.' – Planar Electrodes.
Current / Potential Output from P/Stat.

Electrode : Planar Titanium (1·0 cm.^{2}).

Electrolyte : 3·5M. $FeCl_2$.

pH = 0·5.

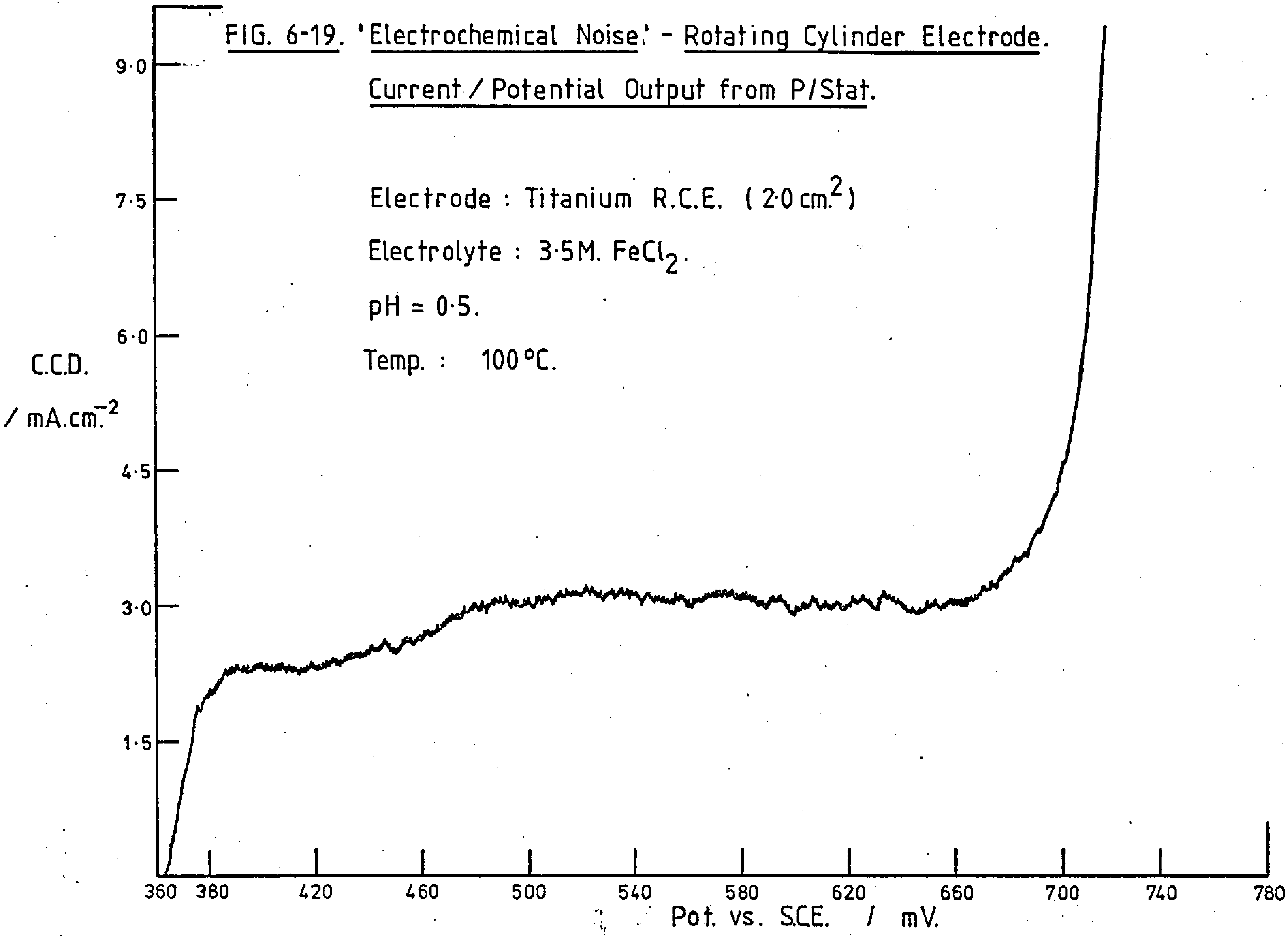


FIG. 6-19. 'Electrochemical Noise.' - Rotating Cylinder Electrode. Current / Potential Output from P/Stat.

Electrode : Titanium R.C.E. (2·0 cm.^{2})

Electrolyte : 3·5M. $FeCl_2$.

pH = 0·5.

Temp. : 100 °C.

FIG. 6-20. Cathodic Polarisation - Effects of Ferric Ion Build-Up.

Electrolyte : 3·5M. $FeCl_2$.

Temp. : 30°C.

pH = 0·5.

FIG. 6-21. Cathodic Polarization - Effects of Temperature.

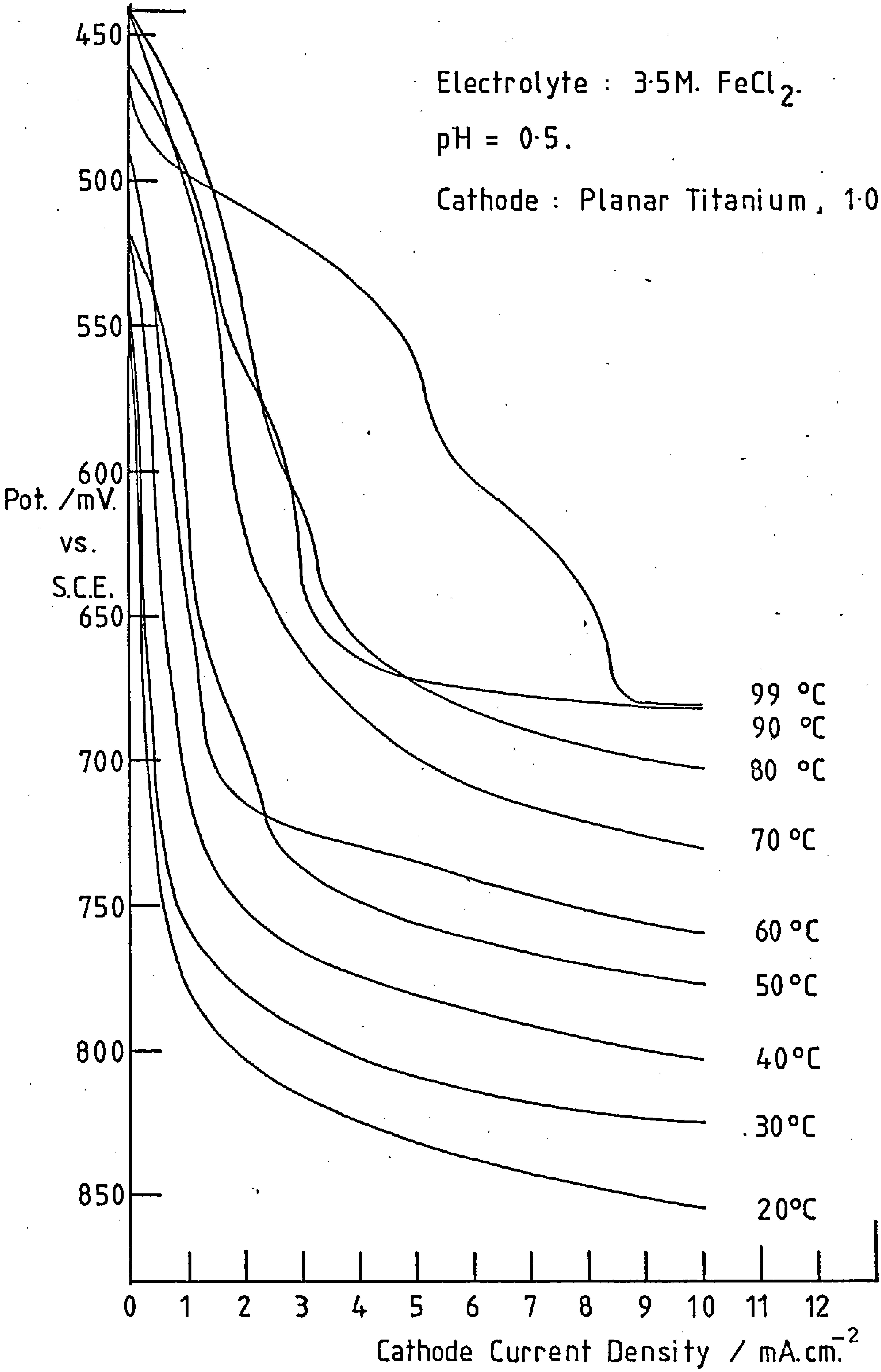


FIG. 6-22. Anodic Polarization - Titanium.

FIG. 6-23. Anodic Polarization - Stainless Steel.

FIG. 6-24. Anodic Polarization - Platinised Titanium.

Electrolyte : 3·5M. $FeCl_2$.

pH = 0·5.

Temp. : 50°C.

FIG. 6-25. Anodic Polarization. - Graphite.

Electrolyte: 3·5M. $FeCl_2$.

pH = 0·5.

Temp.: 50°C.

FIG. 6-26. Summary of Anodic Polarization Data.

Electrolytes : All 3·5M. Fe^{2+}

pH = 0·5.

Temp. : 50°C.

FIG. 6-27. Cathodic Polarization of Iron in a Mixed (20:1) Chloride-Sulphate Electrolyte.

Electrolyte : 3·5M. $FeCl_2$.

pH = 0·5.

Temp. : As Shown.

Electrode : Planar Titanium. (1·0cm^2

FIG. 6-28. Cathodic Polarization - Using Stainless Steel R.C.E.

FIG. 6-29. Cathodic Polarization - Successive Runs in Electrolyte at pH = 1·0.

FIG. 6-30. Variation of Cathode Current Efficiency / Number of Coulombs Passed through Cell.

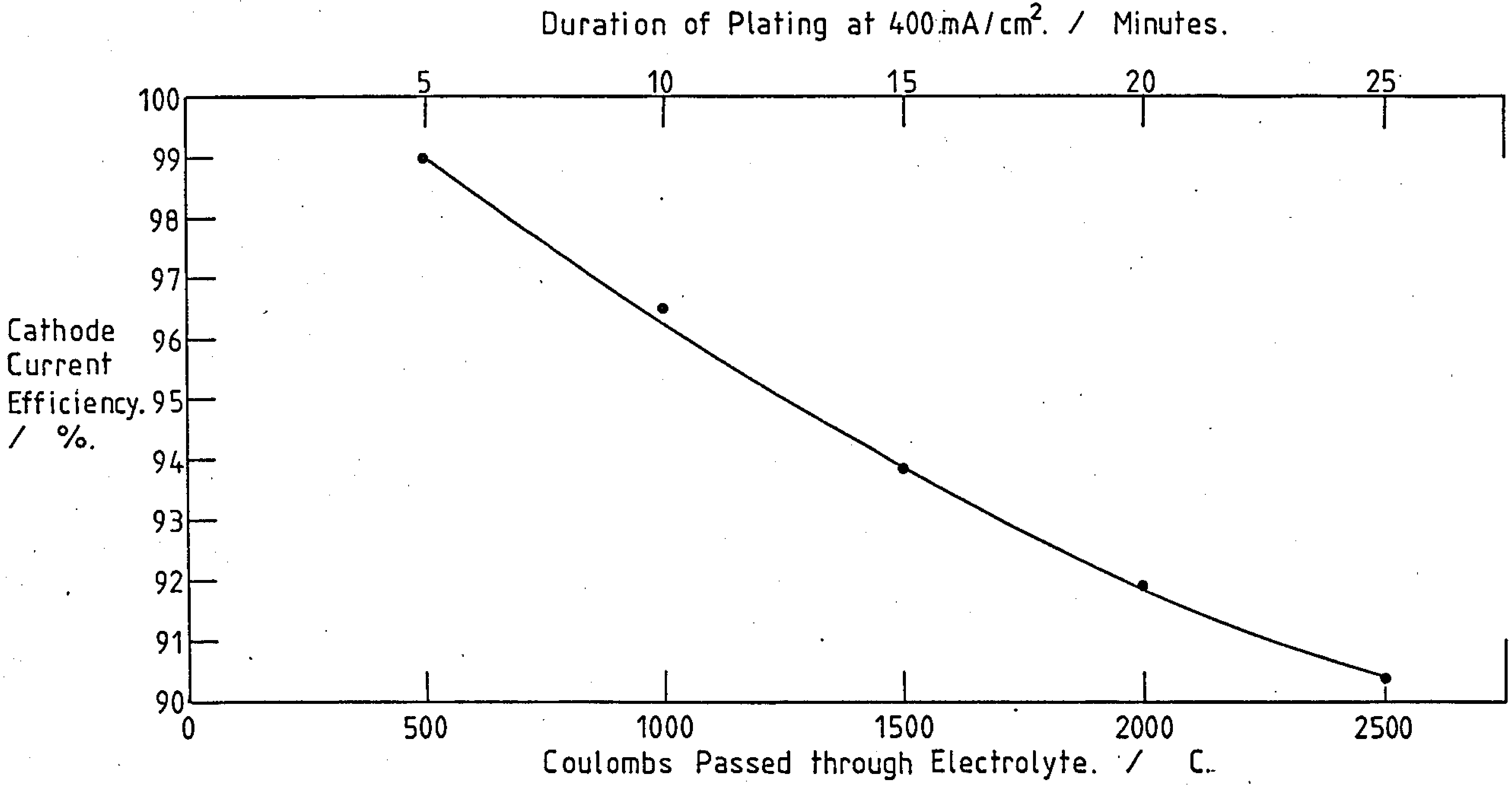


FIG. 6-31. Build-Up of [Fe(III)] with Number of Coulombs Passed through Cell.

FIG. 6-32. Cathodic Polarization - Electrolyte Pre-reduced with Hydrazine Dihydrate.

FIG. 6-33. Effect of 0·025M Hydrazine Dihydrochloride on [Fe(III)] in 3·5M. $FeCl_2$.

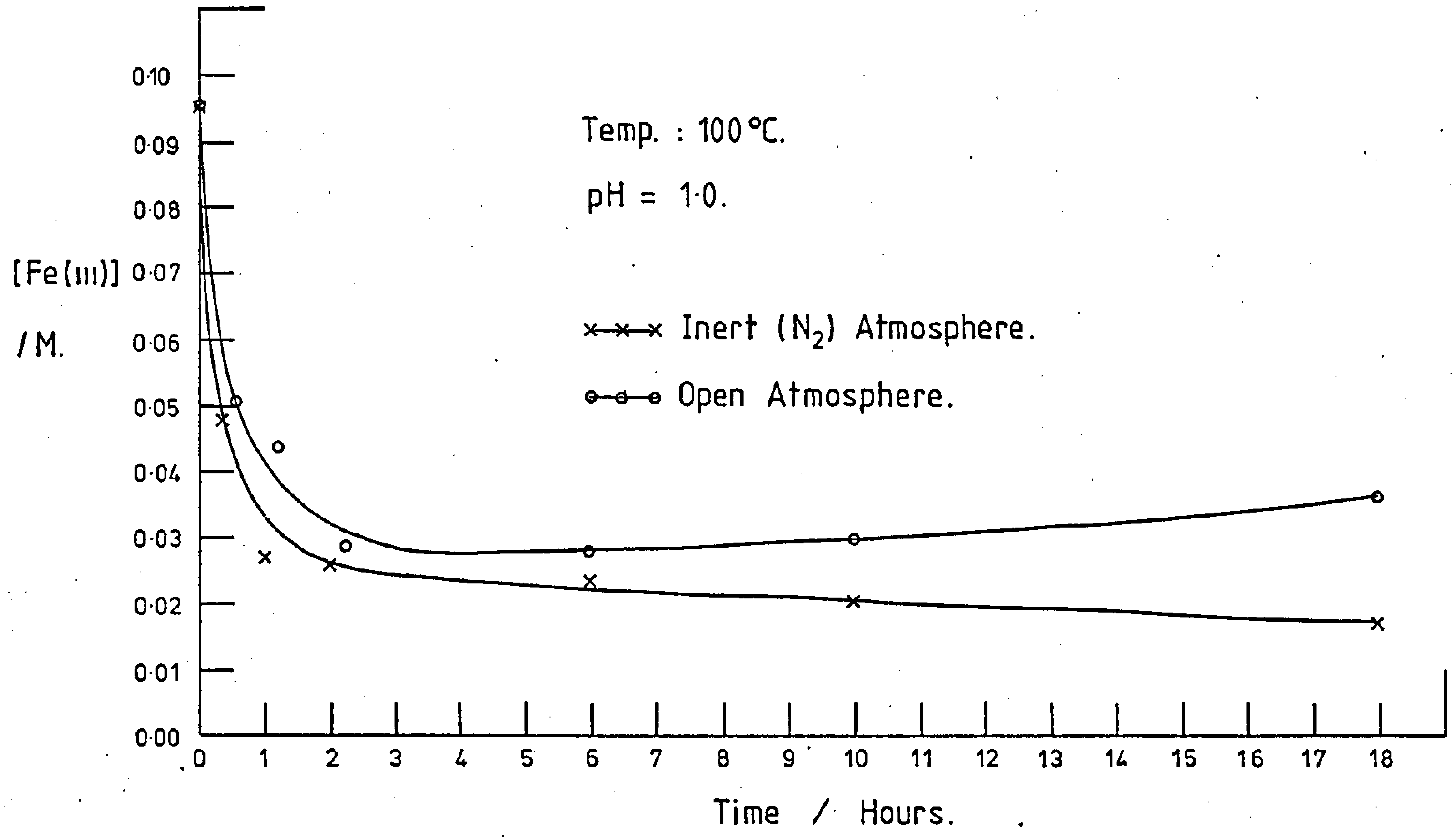


FIG. 6-34. Effect of Hydrazine Dihydrochloride on [Fe(III)] During Electrodepn. at 200 mA.cm^{-2}.

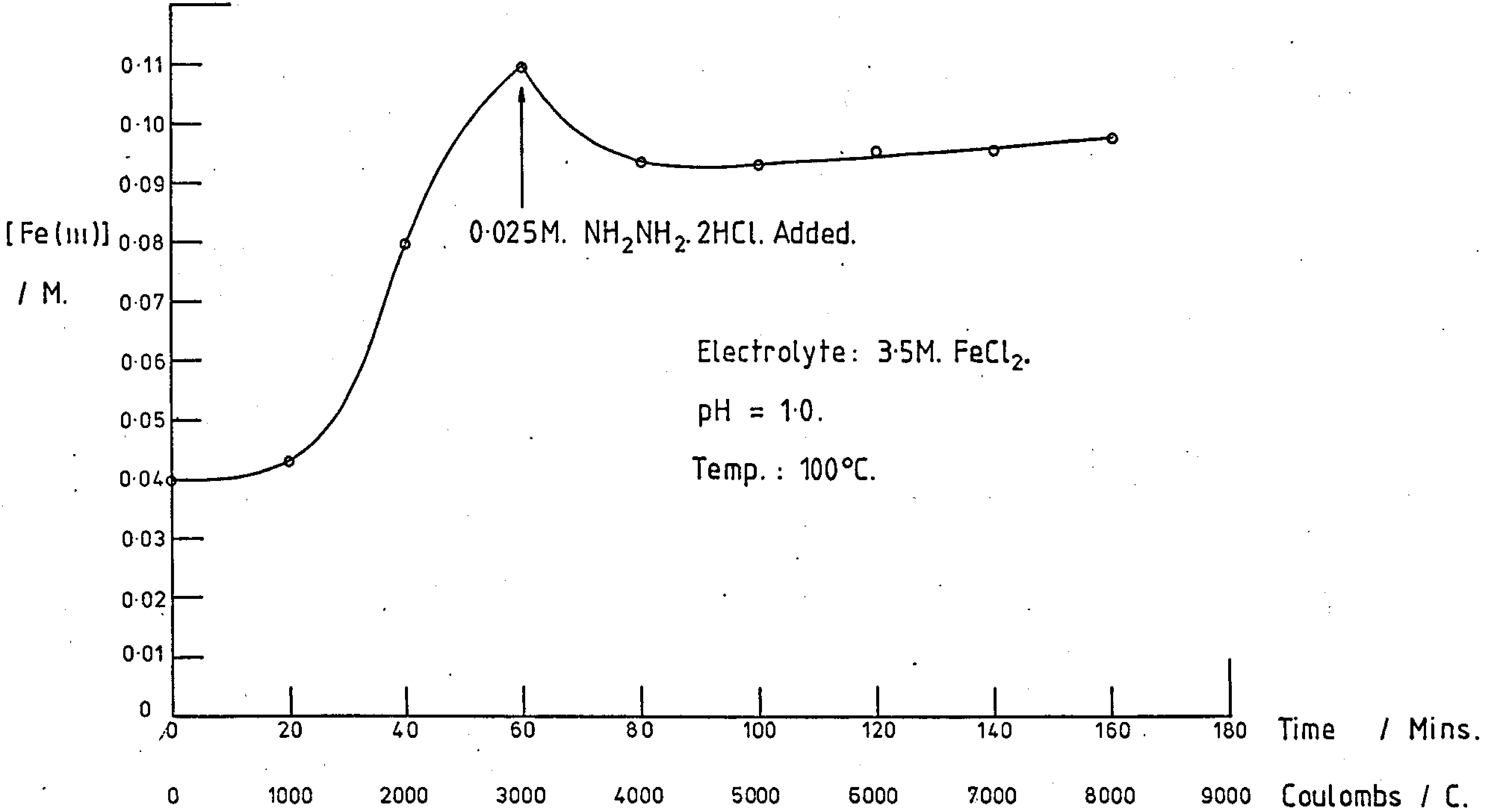


FIG. 6-35. Effect of Ion-Exchange Membrane on Cell Voltage Requirements.

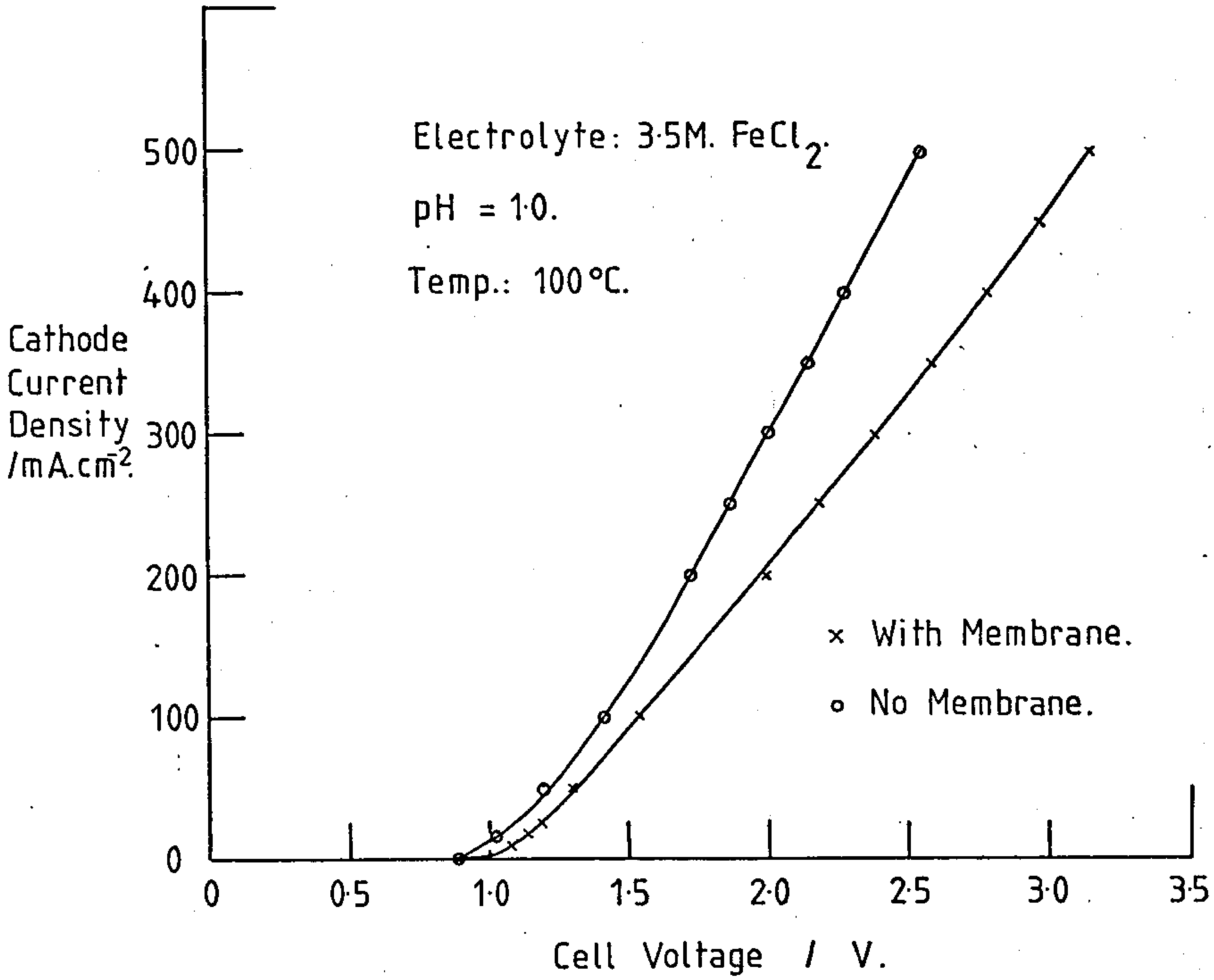


FIG. 6-36. Cathodic Polarization - Typical Result Using Divided Cell.

FIG. 6-37. Electrochemical Reduction of Fe(III) in Divided Cell.

FIG. 6-38. Cathodic Polarization of Iron in 3·5M. $FeCl_2$ with Addition of Cationic Surfactant (Monflor 73, I.C.I. Chems. Ltd.)

FIG. 6-39. Cathodic Polarization of Iron in 3·5M. $FeCl_2$ with Addition of a Non-Ionic Surfactant ('Texofor N.12.' A.B.M. Chems. Ltd.)

FIG. 6-40. Cathodic Polarization of Iron in 3·5M. $FeCl_2$ with Addition of an Anionic Surfactant. ('Fluorad FC-95'. 3M. Ltd.)

TABLE 2.1

EARLY CHLORIDE ELECTROLYTE

INVESTIGATOR (REF.)	DATE	ELECTROLYTE	ACIDITY	CURRENT DENSITY (A/m^2)	TEMP. °C	REMARKS
Thiele (48)	1891	Ferrous chloride, 400 g/l	50 m Glacial acetic per l	-	Room	Deposit contained 0.0048-0.075% Sulphur
Hicks and O'Shea (49)	1895	Ferrous Chloride + 5% NH_4CL	Neutral	15-17	Room	Very pure deposit
Ryss and Bogomolny (50)	1906	Ferrous chloride 1000g + 1000ml water	-	40	60-70	-
Kern (51)	1908	Ferrous chloride 285g NaCl,102g; Dil. to 1000mℓ	10mℓ Conc^n HCl per l	110-220	20+50	Deposit superior to sulphate baths
Muller (52)	1909	Ferrous chloride 300 g/l	-	70	Room	As above
Cain, Schramm + Cleaves (53)	1916	Ferrous chloride 250-300 g/l	Neutral	50-70	Room	No agitation. Used porous cups. Impurities 0.024-0.026%.
Cain, Schramm + Cleaves (53)	1916	Ferrous chloride, 233g; NaCl, 103g; water to 1 l	Neutral	30-40	Room	Larger scale than above. Impurities 0.033%

TABLE 2.1 (cont/d)

INVESTIGATOR (REF.)	DATE	ELECTROLYTE	ACIDITY	CURRENT DENSITY (A/m^2)	TEMP. °C	REMARKS
Vie (54)	1919	Ferrous chloride, 285 g; NaCl, 102g water to 1 l	-	160	50-70	Product over 99.9% iron
Hineline (55)	1923	Ferrous chloride + calcium chloride, equal parts saturated at 30°C	-	-	<100°C	For deposit or irregular shaped articles
Duhme (56)	1924	Ferrous chloride + magnesium choride	No acid added	100	<100°C	Special all. Product 99.994% iron
Merck (57)	1900	Ferrous chloride only	-	300 to 400	70°C	Agitation necessary for iron refining
Fischer-Langbein (8-14)	1908	Ferrous chloride, 450g; $CaCl_2$, 500g, water 750 ml	No acid added	1000 to 2000	90-110	High purity deposit H content low
Kelsen (58)	1928	Ferrous chloride, calcium chloride, Potassium chloride	-	-	-	Greater concentration using two salts

TABLE 2.2

EARLY SULPHATE ELECTROLYTES

INVESTIGATOR (REF.)	DATE	ELECTROLYTE	CURRENT DENSITY (A/m^2)	TEMP. °C	REMARKS
Klein (59)	1967	$FeSO_4$ 50 g $MgSO_4$ 50 g Water 1000 mℓ	10-20	Room	Deposits for 'steel facing
Hoepner and Klie (60)	1895	$FeSO_4$ 467 g $(NH_4)_2SO_4$ 759 g Water 1500 g	300	70-80°C	Thin deposits (Used porous diaphragm)
Neuburger and Von Klobukov (61)	1890	Ferrous Sulphate and Ammonium Oxalate	-	-	For analytical purposes
Skrabal (62,63)	1904	Ferrous Ammonium Sulphate	-	Room	Pure iron for standardising solutions
Burgess and Hambuechen (5)	1904	Ferrous Ammonium Sulphate	65-85	-	For iron refining. Product 99.99% pure iron
Maximowitsch (64)	1905	$FeSO_4$ 200 g/ℓ	30	Room	For 'steel' facing

TABLE 2.2 (cont'd)

INVESTIGATOR (REF.)	DATE	ELECTROLYTE	CURRENT DENSITY (A/m^2)	TEMP. °C	REMARKS
Lee (65)	1906	Ferrous Sulphate (saturated at 20°C)	200	90°C	Bath covered in paraffin. Solution agitated
Ryss and Bogomolny (50)	1906	Ferrous Ammonium Sulphate 70 g/ℓ	50	Room	Higher temperatures gave poor results
Amberg (66,67)	1908	Ferrous Ammonium Sulphate 182 g/ℓ	2o-65	Room	Agitation necessary at higher temperatures
Kern (51)	1908	Ferrous Sulphate 40 g/ℓ	110-220	20 and 50°C	Good deposit, but inferior to chloride
Kern (51)	1908	$FeSO_4$ 300 g/ℓ Na_2SO_4 210 g/ℓ	110-220	20 and 50°C	As above
Pfaff (68)	1910	2 N. $FeSO_4$	200	70°C	Iron containing less than 0.001% sulphur

TABLE 2.3

MIXED SULPHATE-CHLORIDE ELECTROLYTES

Investigator (Ref)	Date	Electrolyte	Current Density A/m^2	Temperature	Remarks
Meidinger (83)	1859	$FeSO_4$, 900g NH_4Cl 450g water 4	-	Room	Used for "steel facing"
Varrentrapp (84)	1868	$FeSO_4$ 1800g NH_4Cl 1350g Water 13.5	10-20	Room	Used for "steel facing"
C. F. Burgess (85	1911	$FeSO_4$ 200g NH_4CL 40g Water to 1	70-110	Room	99.97% pure deposits
Watts + Li (86)	1914	$FeSO_4$ 150g NH_4Cl 40g Water to 1	110	Room	For iron refining
Arzano + Clerici (Brit. Pat. 114,305)	1918	$FeSO_4$ 40 parts NH_4Cl 50 parts + water	-	100-105°C	For iron refining
Shepherd + Brazil (Brit. Pat. 119,200)	1918	$FeSO_4$, NH_4Cl, KB_r, + Iron metal + H_3BO_3	-	-	Gen. iron electroplating

Table 5.1

Chemical Etches For Titanium

	Chemical	Quantity	Reference
1.	Concentrated Nitric Acid	40%	J.B. Cotton + P.C.S.
	Concentrated Sulphuric Acid	30%	Wayfield
	40% Hydrofluoric Acid	30%	Trans. I.M.F. 45 (1967), 48
2.	40% Hydrofluoric Acid	150 cm^3	Metals
	Ferric Chloride	30 g	Handbook (Amer. Soc. of Metals)
3.	0.1% Phosphoric Acid	—	Metals Handbook
	(Electrochemical Etch)		(Amer. Soc. of Metals)

TABLE 7.1

PHYSIO-CHEMICAL PROPERTIES OF POSSIBLE 'CONDUCTIVITY SALTS'

SALT	EQUIVALENT CONDUCTIVITY $\Omega^{-1} cm^{2} mol^{-1}$	SOLUBILITY g/100 cm^{3} water	COMMENT
Sodium Chloride	Na^{+} 50.11 Cl^{-} 76.34	35.7 cold 39.1 hot	Relatively limited solubility
Potassium Chloride	K^{+} 73.50 Cl^{-} 76.34	4.17 mol/ℓ in cold water	stable
Ammonium Chloride	NH_4^{+} 73.4 Cl^{-} 76.34	29.7 cold 75.8 hot	stable
Magnesium Chloride	$\frac{1}{2}Mg^{2+}$ 53.06 Cl^{-} 76.34	167 cold 367 hot	stable
Calcium Chloride	$\frac{1}{2}Ca^{2+}$ 59.50 Cl^{-} 76,34	279 cold 536 hot	stable
Aluminium Chloride	$1/3Al^{3+}$ 63.0 Cl^{-} 76.34	3.46 mol/ℓ in cold water	evolves HCl in hot water corrosive and poisonous

TABLE 7.2

COSTS OF POSSIBLE 'CONDUCTIVITY SALTS'

SALT	COST (£/kg) (1981 BULK WHOLESALE PRICES)
Sodium Chloride	0.14
Calcium Chloride	0.75
Ammonium Chloride	0.26
Potassium Chloride	0.54
Magnesium Chloride	1.34
Aluminium Chloride	∿ 2.00
Ferrous Chloride	∿ 0.70

TABLE 7.3

FERRIC ION CONCENTRATION DURING ELECTRODEPOSITION IN THE DIVIDED CELL

DURATION OF ELECTRODEPOSITION AT 200 mA/cm^2 (MINS)	FERRIC ION CONC^N (M)
0	0.051
30	0.055
60	0.053
90	0.050
120	0.057
150	0.057
180	0.053

TABLE 7.4

CATHODE CURRENT EFFICIENCY AT VARIOUS CURRENT DENSITIES IN DIVIDED CELL

Current Density mA/cm^2 (A/m^2)	C.C.E. %
200 (2000)	98.0 ± 1.0
300 (3000)	98.6 ± 1.0
400 (4000)	99.6 ± 1.0
500 (5000)	98.9 ± 1.0

TABLE 7.5

CATHODE CURRENT EFFICIENCY AT VARIOUS CYLINDER ROTATIONAL VELOCITIES

R.C.E. RATE OF ROTATION (r.p.m.)	C.C.E. % at 400 mA/cm^2
0	98.3 ± 1.0
300	99.0 ± 1.0
600	98.7 ± 1.0
900	98.3 ± 1.0
1200	98.5 ± 1.0

TABLE 7.5

CATHODE CURRENT EFFICIENCY AT VARIOUS CYLINDER ROTATIONAL VELOCITIES (D)

R.C.E. RATE OF ROTATION (r.p.m.)	C.C.E % at 400 mA/cm^2
0	98.3 ± 1.0
300	99.0 ± 1.0
600	98.7 ± 1.0
900	98.3 ± 1.0
1200	98.5 ± 1.0

PLATE 1. General Arrangement of
Laboratory-Apparatus.

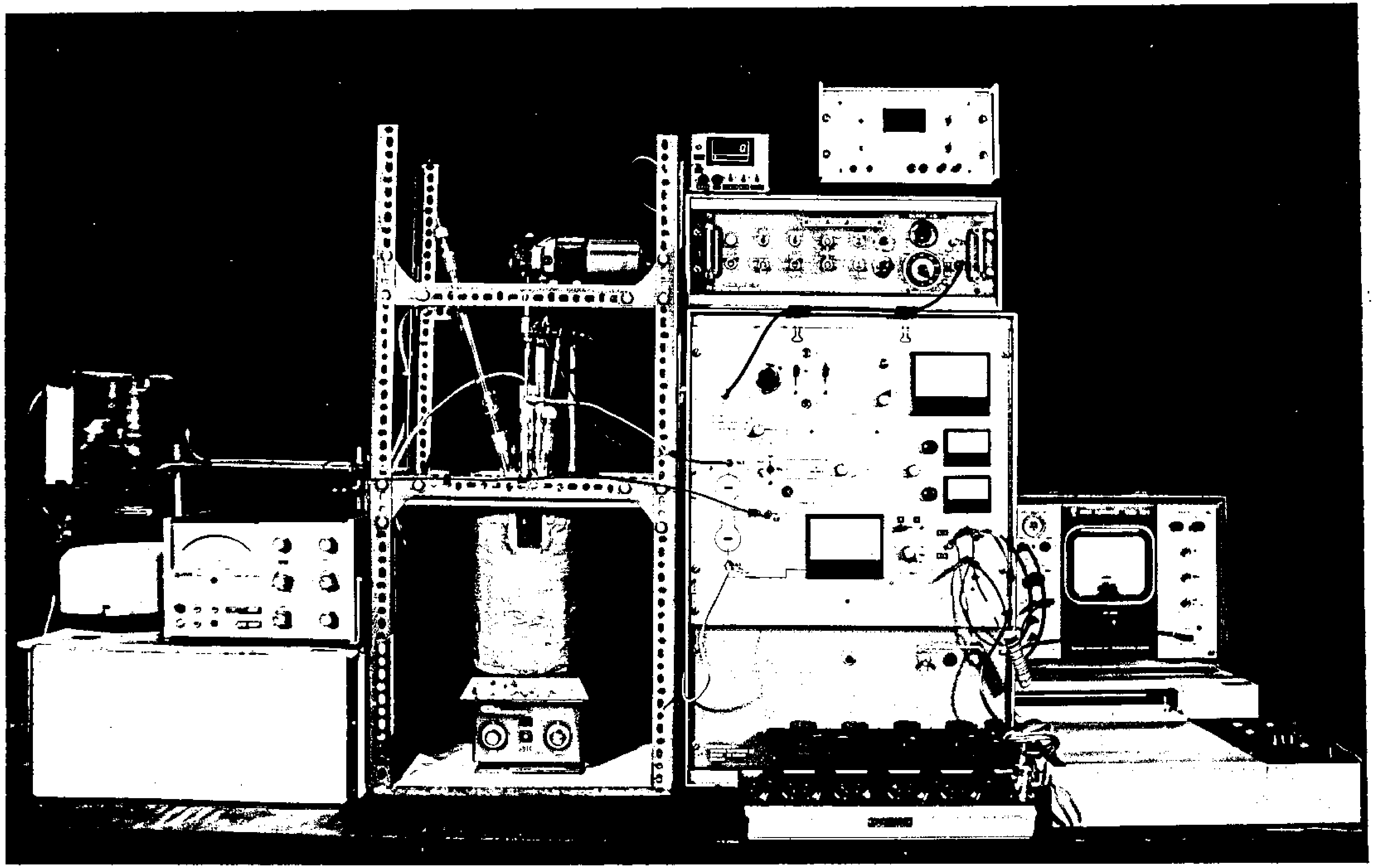


PLATE 2. Laboratory Electrolytic Cell.

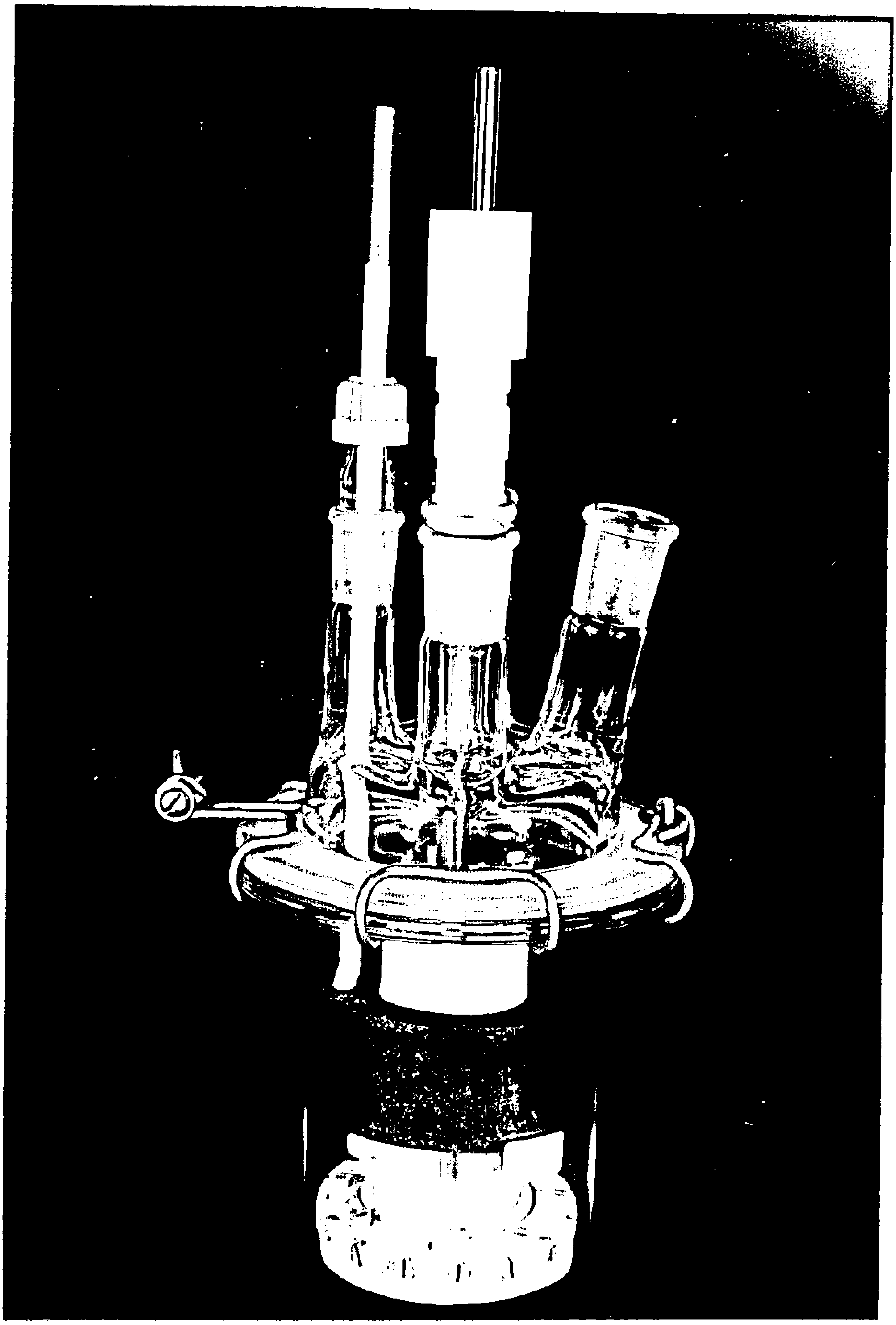
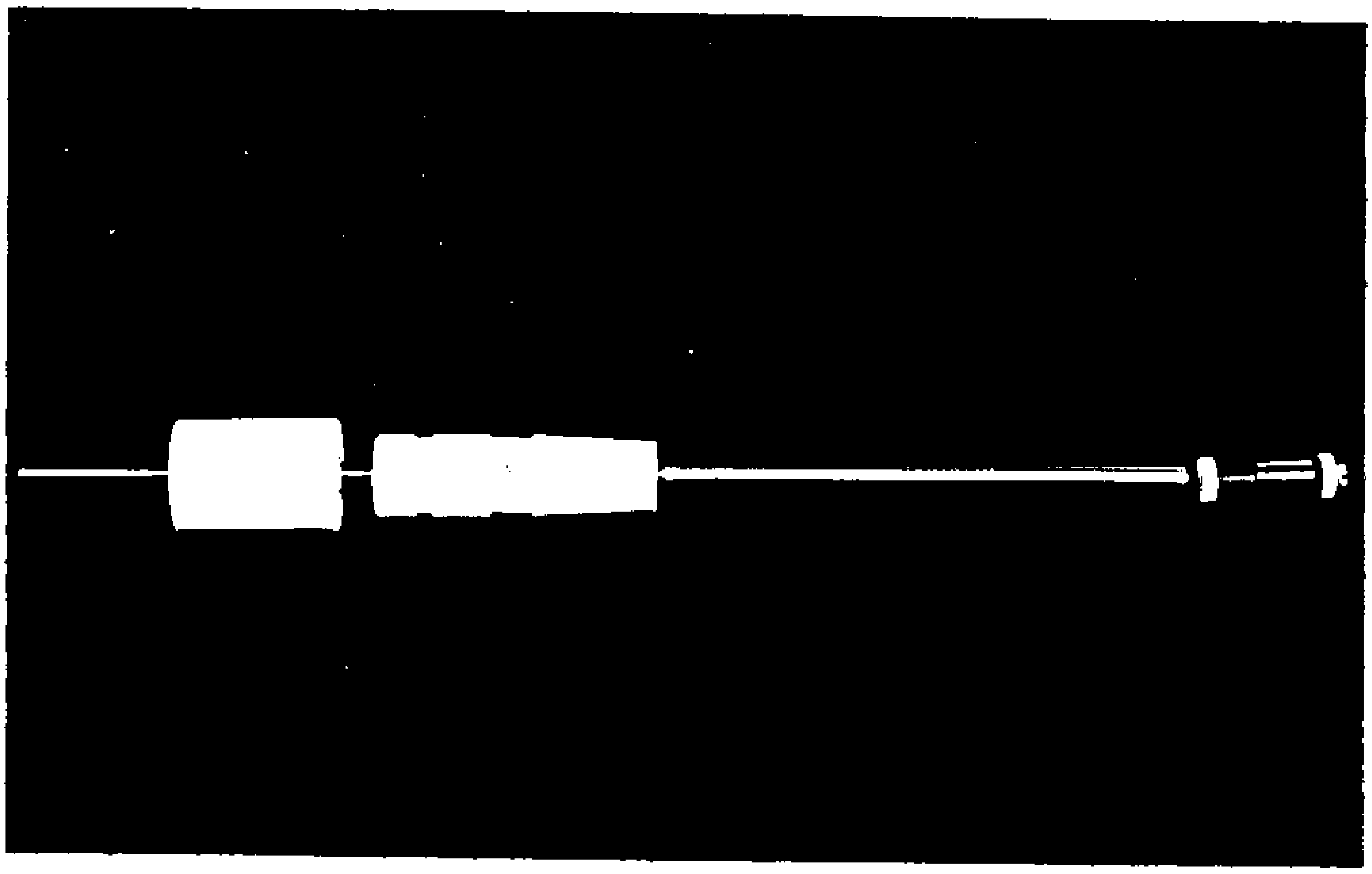
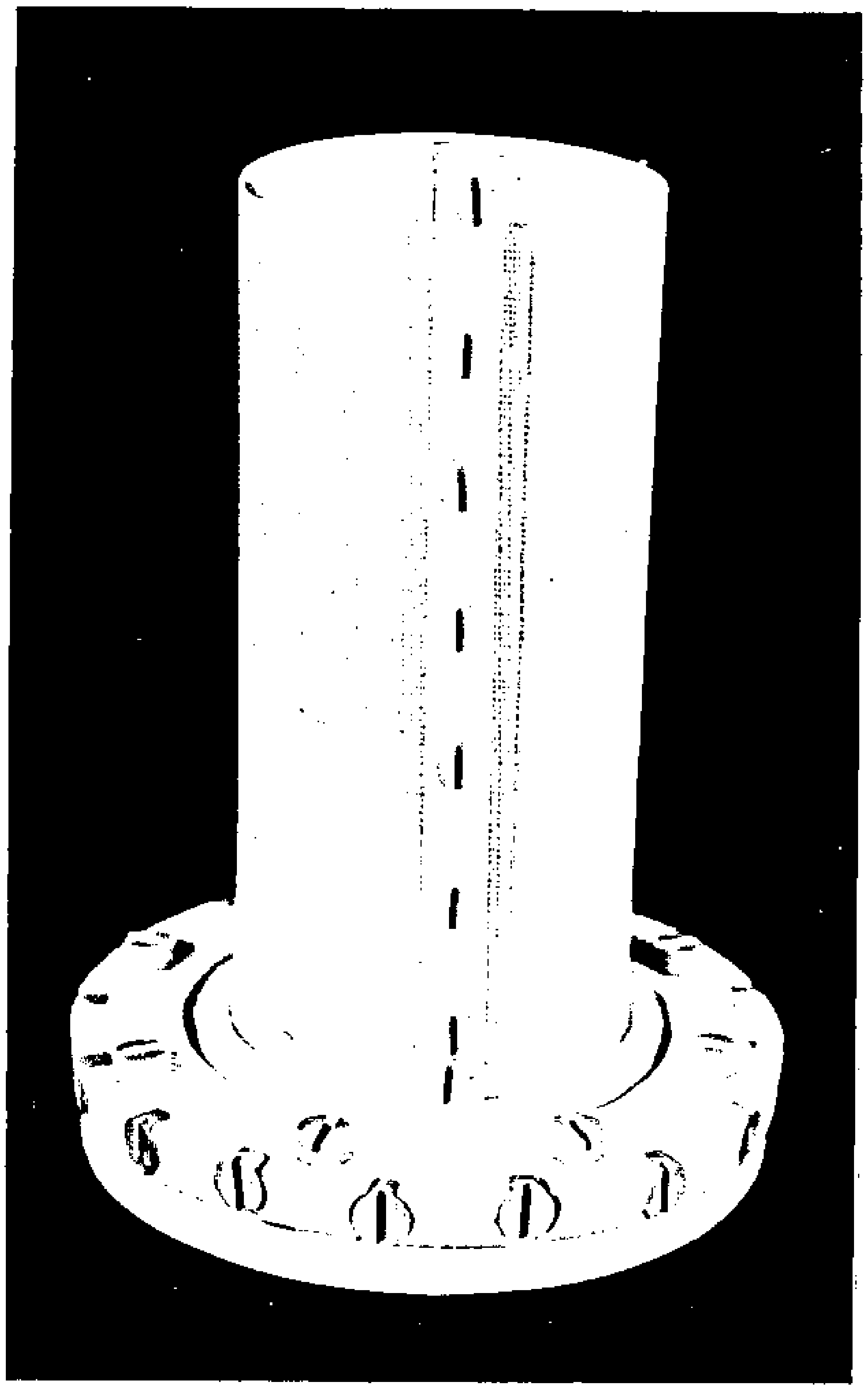


PLATE 3. Rotating Cylinder Electrode Assembly.

PLATE 4. Ion Exchange Membrane Assembly
for Divided Cell.





APPENDIX 1

Regeneration of 'Spent' Ferrous Chloride Electrolyte

Restoration of ferrous ion concentration and reduction of ferric ion concentration is theoretically possible by the following regeneration reactions involving iron metal.

A. $Fe \rightarrow Fe^{2+} + 2e^-$

$2H + 2e^- \rightarrow H + H \rightarrow H_2$

Overall: $Fe + 2H^+ \rightarrow Fe^2 + H_2$ .... Equation 1

B. $Fe \rightarrow Fe^{2+} + 2e^-$

$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

Overall: $2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$ .... Equation 2

C. $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

$H_2 \rightarrow 2H^+ + 2e^-$

Overall: $2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+$ Equation 3

Examination of the oxidation potentials for the half reactions shown enables a prediction to be made whether reaction (1), (2) and (3) are theoretically possible.

Half Reactions in A.

$Fe \rightarrow Fe^{2+} + 2e^-$ $E^o_{298} = -0.440V$

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$ $E^o = \pm 0.000V$

These half reactions can be combined to give the overall reaction:

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$ $E_{298} = -0.440V$

The oxidation potentials vary according to the Nernst equation:

$$E = E^{o} + \frac{RT}{nF} \ln\frac{[Ox]}{[Red]}$$

where: E^{o} is the standard potential for the system

E is the potential under the conditions of the reaction

R is the gas constant

T is the absolute temperature (K)

n is the number of electrons involved in the process

F is the Faraday constant.

Applying this to the half reactions in Section A under typical reaction conditions i.e. 3.5 M $FeCl_2$, pH 1.00, Temperature 100°C, Fe^{3+} 0.03 M we have:

$$E_{Fe^{2+}/Fe} = -0.440 + \frac{8.312 \times 373}{2 \times 96500} \times 2.303 \log_{10} \frac{3.5}{1}$$

$$E_{Fe^{2+}/Fe} = -0.440 + 0.016 = -0.424V$$

$$E_{H^{+}/H} = 0.000 + \frac{8.312 \times 373}{1 \times 96500} \times 2.303 \log_{10}\left(\frac{AH}{P_{H_2}}\right)^{\frac{1}{2}}$$

Assuming $P_{H_2} = 1$, $A_{H+} = 0.1$

$$E_{H^{+}/H} = 0.000 + (-0.074) = -0.074 \text{ V}$$

Hence $Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$ $E = -0.350$ V

The overall potential for the reaction is negative so the above reaction will proceed from left to right.

Half Reaction in B.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad E^o_{298} = -0.440\ V$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^o_{298} = +0.771\ V$$

Thus:

$$2Fe^{3+} + Fe \quad 3Fe^{2+} \qquad E_{298} = -1.211\ V$$

Considering the reaction conditions mentioned previously,

$$E_{Fe^{2+}/Fe} = -0.424\ V$$

$$E_{Fe2+/Fe^{2+}} = E^o{}_{Fe^{3+}/Fe^{2+}} + \frac{RT}{nF}\ \ln \frac{A\ Fe^{3+}}{A\ Fe^{2+}}$$

$$= +0.771 + \frac{8.312 \times 373}{96500} \times 2.303 \log_{10} \frac{0.03}{3.5}$$

$$E_{Fe^{3+}/Fe^{2+}} = +0.618\ V$$

Hence for the reaction:

$$2Fe^{3+} + Fe \rightleftarrows 3Fe^{2+} \qquad E = -1.042\ V$$

The overall potential for the reaction is negative so the above reaction will proceed from left to right.

Similarly for C

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^o_{298} = +0.771\ V$$

$$\tfrac{1}{2}H_2 - e^- \rightarrow H^+ \qquad E^o_{298} = 0.000\ V$$

Thus:

$$2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+ \quad E_{298} = -0.771\ V$$

Hence for the reaction under the conditions previously mentioned:

$$2Fe^{3+} + H_2 \rightarrow 2Fe^{2+} + 2H^+ \quad E = -0.697\ V$$

Again the overall potential for the reaction is negative so the above reaction will proceed from left to right. Hence it can be seen by a consideration of the oxidation potentials, reaction (1) (2) and (3) are likely to occur. However, oxidation potentials measure energy differences only and give no indication of the reaction kinetics. Certain reactions while energetically favourable do not take place to a signicant extent because of unfavourable mechanisms, or the kinetics of the reaction may be extremely slow so little reaction is observed.

APPENDIX 2

SCANNING ELECTRON MICROGRAPHS OF IRON ELECTRODEPOSITS

A number of iron foil deposits were examined using a Jeol Scanning Electron Microscope. Many workers (see Review Sections of this thesis) have made detailed studies of the deposit structure and the effect of various electrolyte parameters on the microstructure. Thus a detailed analysis of this aspect of iron electroforming has not been considered during this project. Some examples of the microgrpahs are included to give a general idea of the nature of the deposit.

Plates 5 and 6 show a typical deposit obtained from a hot (100°C), acidic (pH 1.0) and concentrated (3.5 M) ferrous chloride electrolyte with no addition agents present. The deposit can be seen to consist of a angular crystals with an average diameter of approximately 2 - 4 μm. This structure was typical of all those examined.

Plate 7 shows an example of the foil after it had been exposed to the effects of atmospheric oxidation for some weeks. The effect of corrosion can be clearly seen to have reduced the sharp edges of the crystals to the rounded nodular appearance associated with oxidation products.

The occurrence of pores and pinholes in the electrodeposit is significant in foil production and has been discussed in this thesis. Plate 8 shows what may be an inclusion in the foil surface. Plates 9 and 10 show an example of a pore in the cathode face of the deposit. These and other similar micrographs indicate that the most likely possible causes of 'pinholing' in iron foil is either the inclusion of material into the deposit surface from either the electrolyte or residues on the substrate. No examples of pores caused by gas bubbles were found, even though hydrogen is evolved during the deposition process. It would appear that powerful turbulence during electrodeposition is sufficient to remove any gas formed, from the surface of the deposit.

The cathode face of the electroform is illustrated in Plates 11 and 12. As evidenced by the linear scratch marks on the surface, this face of the deposit closely replicates the substrate. The lines are abrasion marks on the cathode surface resulting from preparation of the cathode with fine emery paper.

PLATE 5. Typical Iron Electrodeposit.

Magnification: 500X.

PLATE 6. As Above. Magnification : 2000X.

PLATE 7. Corroded Iron Electrodeposit.

Magnification : 1500X.

PLATE 8. Example of Possible Inclusion in the Electrodeposit. Magn. : 5000X.

PLATE 9. Pore in the Cathode Face of the Electrodeposit. Magn. : 1000X.

PLATE 10. As Above. Magnification : 8000X.

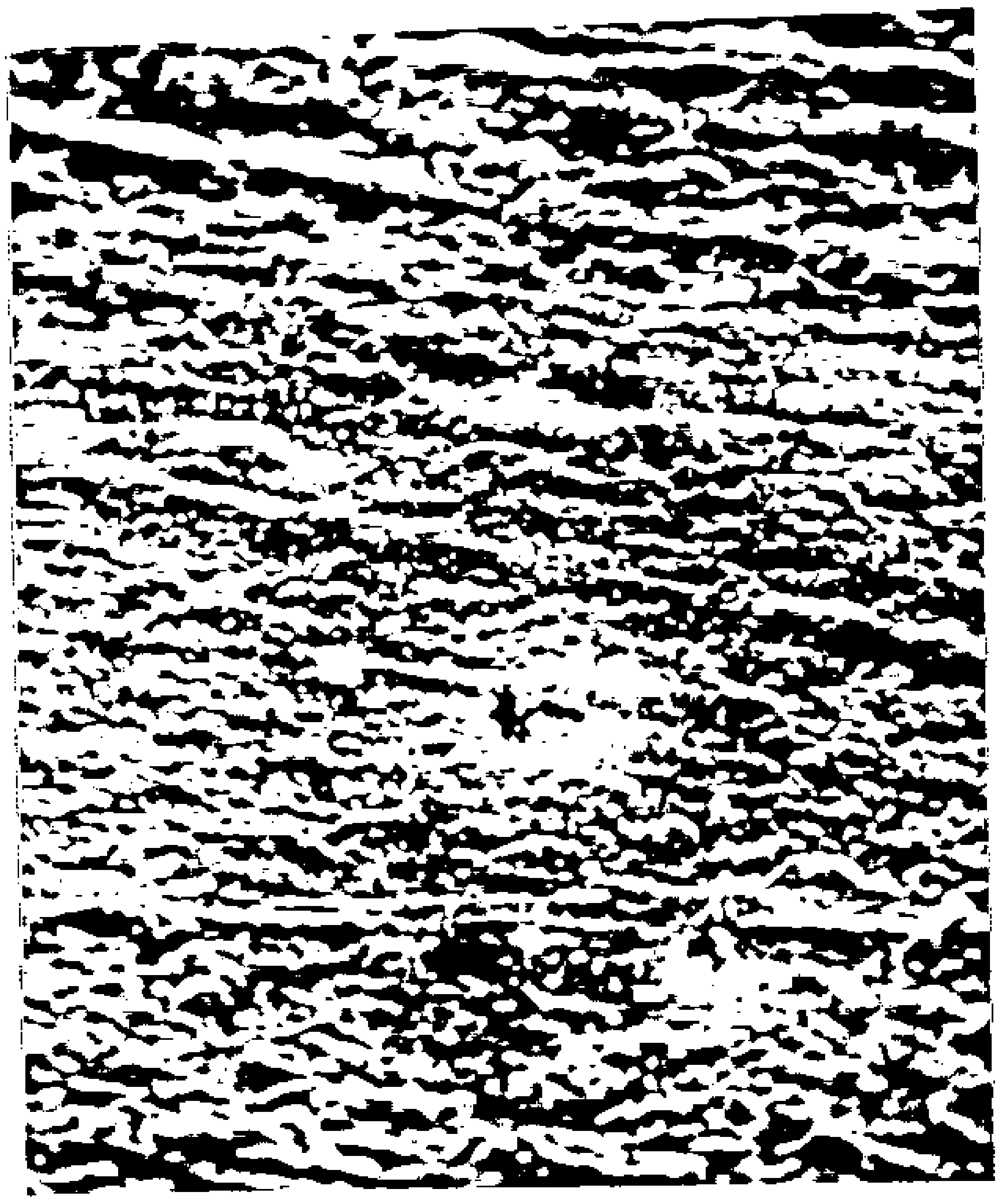


PLATE 11. Cathode Face of Electrodeposit.

Magn. : 300X.

PLATE 12. As Above. Magn. : 800X.