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DEPT OF MECHANICAL ENGINEERING E A FLETCHER ET AL.
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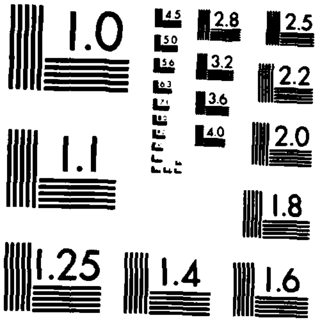

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Edward A. Fletcher, Frank J. Macdonald, and Dennis Kunnerth

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(Received April 8,1985)

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Early in the 19th century, zinc was extracted by reduction of its oxide with coal at temperatures above its boiling point(1180K). Zinc vapor was then condensed in a complicated, air-free system. The overall reaction ZnO + C ---> Zn + CO consists of two concurrent processes:

$$ZnO + CO \longrightarrow Zn + CO_2$$

and

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The first reaction is very fast above 1150K; the second is slow below 1350K.[3]

During World War I, electrolytic production methods were developed in the United States and Canada. Electrolysis produces a very pure product. The ore is first acid-leached to produce the electrolyte $ZnSO_4$. The theoretical decomposition potential for $ZnSO_4$ is 2.35 volts, but cells are run at about 3.6 volts in practice. Current densities are about 0.03 amps/cm^2, and the operating temperature is 308K. The process requires cooling.[4]

The suggestion that sunlight be used as a source of process heat and that the electrolysis be conducted at much-higher-than-conventional temperatures evokes many questions. The problems encountered in working at high temperatures while interfacing with concentrated solar energy have not been adequately investigated. The selection of suitable materials for containment and electrodes and the determination of effective apparatus configurations and operating procedures have not yet been addressed.

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Prepared for Publication

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University of Minnesota
Mechanical Engineering Department
111 Church St. S.E.
Minneapolis, MN 55455

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with the process heat supplied by a fusion reactor.[5,6] The U.S. Bureau of Mines has been involved since the early 1960's with extracting rare earth and uranium metals from their oxides,[7] and, more recently, has been working on the electrolysis of zinc chloride at 773K.[8] In Japan, Hidehiko has studied electrolysis in fused salts[9] and several Soviet investigators have been working with electrolysis in molten hydroxides and phosphates, including electrolysis of ZnO.[10,11]

The largest source of information on high temperature electrolysis is the aluminum industry. The Hall Process has been studied for almost 100 years. Transport properties, electrical properties, electrode reactions and the effect of each on metal production are all available in the literature.[12-14] Moreover since our analytical study had identified ZnO as a potentially interesting subject for such a study, we chose to study the electrolysis of ZnO in a solar furnace for the purpose of discovering appropriate solvents and electrode materials, identifying problem areas, and conducting exploratory basic research to provide us with a foothold, as well as with experience, to enable us to begin the development of a new technology, one which might permit us to use the intrinsic thermodynamic potential of sunlight effectively.

Figure 1 is a phase diagram taken from Ref. 1 which shows the stable phases of Zn and of ZnO at various temperatures and pressures. Operating with liquid ZnO would have been desirable, but its triple point temperature is above 2200K, where its vapor pressure is above 1 atm. Inasmuch as we have had little experience working with our furnace at superatmospheric pressures, prudence and the desire to avoid damaging our furnace dictated that we conduct our initial experiments at atmospheric pressure.

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Quartz and glass containers are said to survive, with molten fluorides, only short term experiments. This is true. Graphite is better. The high density grades are probably preferable to minimize penetration by the melt. BN allows less penetration but it is expensive and brittle. Molybdenum and monel have also been used satisfactorily as crucibles,[12] so we considered them, as well.

Platinum, molybdenum, and pyrolytic graphite have been used as electrodes in molten fluorides. Bismuth pools have been used, but their useful potential range is much smaller than that of platinum due to the dissolution of bismuth on the anodic side. The use of metallic cathodes can be risky. The metal depositing there from electrolysis may alloy with the electrode and reduce its melting point to below the operating temperature. We selected graphite as a good candidate for the cathode, and experimented with nickel.

We anticipated that graphite would have advantages and disadvantages as an anode. Its chief advantage is that it acts as a depolarizer in the electrolysis; it is consumed by the oxygen to form either CO or CO_2, reducing the decomposition potential and providing process heat. Its consumption is also a disadvantage; it obviates advantage of using high-temperature solar process heat, and it may wear unevenly and disturb the operation of the cell.

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After having done many exploratory experiments in which we used crucibles made of graphite and nickel, and electrodes of graphite, nickel, molybdenum, and platinum, we selected as solvents the $0.87NaF-0.13AlF_3$ eutectic, the $0.67NaF-0.33ZnF_2$ eutectic, and NaOH.

We measured current, voltage, temperature, and the amount of Zn recovered. Our analyses included calculation of the amount of Zn which should have been produced, theoretically, and the decomposition potential, as well as the smallest value of the voltage which would normally be expected to produce electrolysis. The latter is important because it determines the operating voltage and, therefore, the energy required to produce Zn. In reversible systems this voltage is determined from the change in gibbs' function. In real situations decomposition potential must be determined experimentally from current-voltage curves.

When voltage is first applied, ions move toward the electrodes and set up opposing voltages. No current should flow until the voltage reaches the decomposition potential. Then the current should rise sharply. An exemplary current-voltage curve of the sort we measured is shown in Fig. 4. There is no sharp rise starting from zero current. Instead, there is a back diffusion of ions from the electrodes as the voltage is building up, and a flow of energy from the external source, the residual current, is needed to maintain the steady state voltage, even at potentials below the decomposition potential.

At higher currents a substantial internal voltage drop accounts for most of the slope on the rising curve. Extrapolation to zero current would give the thermodynamic decomposition potential, if there were no overvoltage or polarization. Reaction or activation polarization is caused by a slow step in the sequence of individual electrode reactions. This sequence could include adsorption of ions, charge transfer, desorption of molecules and/or reactions such as 2O --> O2. Activation polarization can be caused by one or more slow steps which cause a buildup of intermediate products, creating a back emf, which must be overcome by the external energy source. Thus extrapolation to zero current gives the actual decomposition potential which includes the overvoltages on both electrodes.

Concentration polarization results from by a concentration gradient in the cell. It becomes important at higher current densities, as can be seen in Fig. 5. Measurment of the voltage across the two electrodes always includes an ohmic drop due to the current passing through the cell. It is sometimes advantageous to place a third electrode in the system which will act as observation that, in the aluminum industry, ZnO is regarded as a problem, since it is deposited at the cathode before aluminum and is therefore an impurity in the product.

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Another continuing task of our research was a search for crucibles and other containers within which to contain these solvents, electrodes which would survive in the molten salt a reference to which each working electrode potential can be measured. That is, measuring the anode and cathode potentials relative to the reference electrode will give, when added together, the total cell potential without the additional unknown ohmic drop.

Our research objectives were to learn as much as we could about the problems of operating a solar-electrochemical system by developing an apparatus, define limits, probe possible operating conditions, and to gain as much useful information and insights about the underlying science of the process as we could. Because there was so little experience with such processes, our approach was necessarily Edisonian.

We did a series of preliminary experiments which led to major changes in the reactor and ruled out some materials and procedures which we had anticipated might be useful. Our experiments actually began with attempts to electrolyze Al_2O_3 in cryolite, the well known basis for the Hall Process. The purpose was to provide us with a bench mark as well as a device for initiate us and provide us with an introduction to the problems of working with this new technology. We also intended, in the process of conducting these educational experiments, to quickly explore the use of readily available, inexpensive materials and simple experimental techniques, even those which seemed only marginally likely to succeed, on the chance that they might provide us with a quick payoff. The information we acquired during the course of these experiments may be helpful to other investigators. We were destined to observe most of the difficulties we have mentioned in connection with electrode materials in the present study, as well as to obtain some useful results.

EXPERIMENTAL PART

Apparatus.

The solar furnace, instrumentation, and the arrangement of reactors in it have been described previously.[22-25]

We know of no previous experimental work in the area of solar high temperature electrochemical production of metals. Our cells evolved over a period of about a year. Almost every experiment was a learning experience which pointed out problem areas and suggested solutions. In the beginning of the research, each experiment guided the design of the next. The cell which finally evolved and was used in most of the experimental measurements is described in this section. It will be instructive to those who contemplate doing related research to review in some detail our experiments and the observations which led to major changes in media, anodes which would survive contact with oxygen, and cathodes which would survive the excellent alloying characteristics of Zn.

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Figure 5 shows a cell in the receiver-cavity. The cavity is enclosed on the incident-solar-flux side by a Pyrex window, a hemispherical dome, cut from a twelve liter round bottom flask, flanged and ground to a flat surface to mate well with the metal outer face-plate of the receiver. It was spring loaded against the face plate. Dow Corning High Vacuum Grease was used as a sealant.

The receiver itself contained two chambers. The forward chamber achieved temperatures as high as 2000K in the present study. It was insulated with a 2.5mm thick zirconia felt cloth, Zircar Products, Inc., ZYF-100, made of 4-5micron diameter yttria-stabilized zirconia fibers. We formed the insulating layer by wrapping the felt around a mandrel. The aperture was formed by wrapping the felt, in varying widths, between two cones.

The chamber which housed the electrolytic cell was insulated with Fiberfrax, an alumina-silica fibrous felt whose continuous use limit is 1530K. The back insulating plug was made of continuously wrapped Fiberfrax felt, 3.5 cm wide, backed by and glued to a rigid Fiberfrax board 2.5cm thick. The reactor shell was a 46cm long, 1cm thick, 31cm diameter 6061-T6 aluminum pipe, welded to 1.6cm thick grooved-for-O-ring aluminum flanges 40cm in diameter. The flanges accommodated 12 bolt holes. The 35.6cm O-rings were made of Viton, a fluoroelastomer said to be useful to about 530 K.

The front and back plates were made of 1.9cm thick 2024-T351 Al bolted to the flanges with 1/4 inch stainless steel bolts. The front plate was an annulus with a 22 cm inner diameter.

The septum between the two inner chambers was a 1.5cm thick graphite disk through which six 3mm holes had been drilled. Its purpose was to help keep solvent vapors from depositing on the cool window, since reducing the clarity of the window would result in its very rapid heating and destruction. To assure that there would be no deposition of condensible materials on the window, we flowed argon through the indicated tube in the bottom of the receiver, through the steel plate which supports the crucible, into the front section of the reactor, and then through the holes in the graphite disk. Radiation from the graphite disk was the principle source of energy transfer to the cell.

The electrolytic cell, shown in detail in Fig. 6, was contained in a graphite case, the crucible. It contained three electrodes: a graphite cathode, where Zn was deposited, a platinum anode, where O_2 was deposited, and the crucible itself, which served as the reference electrode against which the cathode and anode potentials were measured. The anode was surrounded by a graphite shroud which was electrically insulated from the anode and the crucible by BN rings. The shroud kept the product vapors from mixing and recombining. We attached the boron nitride ring separating the anode from the shroud to the anode by sandwiching it between two pieces of graphite which, in turn, were held together by the two halves of the threaded Monel connector. The two sheet metal strips shown attached to the shroud and bent over top of the BN ring permitted the shroud to be raised from the melt along with the anode. The cathode was also electrically insulated from the crucible by the boron nitride ring shown in the figure.

During electrolysis, O_2 formed at the anode flows through the Monel connector, into the graphite anode tube and thence to the atmosphere. Zinc formed at the cathode is swept by the argon through the Monel connector, into the graphite cathode tube and thence to the pyrex condenser and Fiberglas filter, shown in Fig. 5, which collect the zinc.

The connection between the cell and the condenser was made of graded glass. The part deepest inside the reactor was made of quartz, which was graded to Pyrex, where it joined the Pyrex condenser. The filter holder, shown in Fig. 5, was machined of aluminum plate. A fine copper screen supported the filter. The condenser and filter also collected solvent vapor which was being swept out by the argon.

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The experiments were done nominally at ambient pressure, but because blockage by condensation in cool tubes was possible, we monitored the pressure to guard against overpressurization by the flow of argon or the production of O_2.

We used an IBM personal computer for reducing and maniputo 900K.[20,21]

After having done many exploratory experiments in which we used crucibles made of graphite and nickel, and electrodes of graphite, nickel, molybdenum, and platinum, we selected as solvents the $0.87NaF-0.13AlF_3$ eutectic, the $0.67NaF-0.33ZnF_2$ eutectic, and NaOH.

We measured current, voltage, temperature, and the amount of Zn recovered. Our analyses included calculation of the amount of Zn which should have been produced, theoretically, and the decomposition potential, as well as the smallest value of the voltage which would normally be expected to produce electrolysis. The latter is important because it determines the operating voltage and, therefore, the energy required to produce Zn. In reversible systems this voltage is determined from the change in gibbs' function. In real situations decomposition potential must be determined experimentally from current-voltage curves.

When voltage is first applied, ions move toward the electrodes and set up opposing voltages. No current should flow until the voltage reaches the decomposition potential. Then the current should rise sharply. An exemplary current-voltage curve of the sort we measured is shown in Fig. 4. There is no sharp rise starting from zero current. Instead, there is a back diffusion of ions from the electrodes as the voltage is building up, and a flow of energy from the external source, the residual current, is needed to maintain the steady state voltage, even at potentials below the decomposition potential.

At higher currents a substantial internal voltage drop accounts for most of the slope on the rising curve. Extrapolation to zero current would give the thermodynamic decomposition potential, if there were no overvoltage or polarization. Reaction or activation polarization is caused by a slow step in the sequence of individual electrode reactions. This sequence could include adsorption of ions, charge transfer, desorption of molecules and/or reactions such as 2O --> O2. Activation polarization can be caused by one or more slow steps which cause a buildup of intermediate products, creating a back emf, which must be overcome by the external energy source. Thus extrapolation to zero current gives the actual decomposition potential which includes the overvoltages on both electrodes.

Concentration polarization results from by a concentration gradient in the cell. It becomes important at higher current densities, as can be seen in Fig. 5. Measurment of the voltage across the two electrodes always includes an ohmic drop due to the current passing through the cell. It is sometimes advantageous to place a third electrode in the system which will act as lating the data and for storing it on floppy discs and a Bausch and Lomb, Houston Instruments eight pen plotter for plotting the results.

Procedure.

The first step in preparing for an experiment was to load the crucible with solvent and ZnO. The solvent was either freshly prepared, or the recrushed melt from a previous run was used. Enough ZnO was added to insure that the melt would remain saturated. The chemical potential of ZnO in solution was therefore the same as that of the solid. The crucible was then covered, and the electrodes were inserted. Then the crucible was placed in the receiver, the anode and cathode tubes were threaded onto the electrodes, the crucible was connected to the steel plate by nichrome wire, and one thermocouple was inserted into the crucible base. Finally, the insulating plug was inserted and the back plate of the receiver was bolted on.

When it was necessary to take down the reactor the window was removed to avoid damaging it. Before replacing it, we cleaned it, applied a thin layer of vacuum grease, and resecured it to the receiver with the three spring loaded bolts. The leads from the power supply were then attached to the anode and cathode tubes and the condenser and filter were installed. Finally, the system was perfused with argon flowing at about 5 liters/minute.

The heliostat was then set to track with the doors closed. The computer and data logger were turned on. The pyroheliometer turned on. One door was then opened slightly and the pyrometer, which measures the temperature of the front chamber in the reactor, was aligned. The computer was then instructed to log data, and both doors were opened all the way to start heating up the reactor.

As the crucible temperature approached the test temperature, we diminished the power to the receiver by partially closing the furnace doors to slow down the rate of temperature rise. Usually, less than half the available solar power was needed to maintain the test temperature. Once the temperature was steady, we began electrolysis by increasing the voltage across the two working electrodes in appropriate increments. The data logger recorded data every 7 seconds. We took at least three points at each voltage setting. The voltage was increased in this manner to about 4 or 5 volts; then it was decremented to zero. It was then increased slowly to the desired operating voltage, where it remained until the end of the run. During shut-down, it was again reduced slowly to zero.

a reference to which each working electrode potential can be measured. That is, measuring the anode and cathode potentials relative to the reference electrode will give, when added together, the total cell potential without the additional unknown ohmic drop.

Our research objectives were to learn as much as we could about the problems of operating a solar-electrochemical system by developing an apparatus, define limits, probe possible operating conditions, and to gain as much useful information and insights about the underlying science of the process as we could. Because there was so little experience with such processes, our approach was necessarily Edisonian.

We did a series of preliminary experiments which led to major changes in the reactor and ruled out some materials and procedures which we had anticipated might be useful. Our experiments actually began with attempts to electrolyze Al_2O_3 in cryolite, the well known basis for the Hall Process. The purpose was to provide us with a bench mark as well as a device for initiate us and provide us with an introduction to the problems of working with this new technology. We also intended, in the process of conducting these educational experiments, to quickly explore the use of readily available, inexpensive materials and simple experimental techniques, even those which seemed only marginally likely to succeed, on the chance that they might provide us with a quick payoff. The information we acquired during the course of these experiments may be helpful to other investigators. We were destined to observe most of the difficulties we have mentioned in connection with electrode materials in the present study, as well as to obtain some useful results.

EXPERIMENTAL PART

Apparatus.

The solar furnace, instrumentation, and the arrangement of reactors in it have been described previously.[22-25]

We know of no previous experimental work in the area of solar high temperature electrochemical production of metals. Our cells evolved over a period of about a year. Almost every experiment was a learning experience which pointed out problem areas and suggested solutions. In the beginning of the research, each experiment guided the design of the next. The cell which finally evolved and was used in most of the experimental measurements is described in this section. It will be instructive to those who contemplate doing related research to review in some detail our experiments and the observations which led to major changes in

At the end of an experiment, we closed both doors, stowed the heliostat, and reopened the doors to provide good ventilation to the concentrator room. We then disconnected the condenser so that the anode and cathode, with their shrouds, could be raised from the solvent before it froze, and secured them with clamps on top of the reactor. The reactor was then allowed to cool until no vapor could be seen coming from the cathode tube. The argon flow was reduced to about 1 l/min, until the temperature had dropped to 500K, and then turned off.

Figure 8 shows the time history of several variables during an example run. It is evident that the crucible temperature can easily be controlled to within about 10K during the course of an electrolysis, even during periods of varying insolation, by manipulation of the door positions.

The amount of Zn recovered in the condenser and filter was determined by treating them with hydrochloric acid and measuring the amount of hydrogen evolved. The agreement between the yield so measured and that which should have been produced according to the integrated current-time history of a run was often poor. We could usually account for, or at least rationalize, the disparity by attributing it to the loss of zinc by subsequent reaction or alloy formation with an electrode, or by its production by the direct reduction of ZnO by the graphite components of the apparatus. This difficulty notwithstanding, the remaining experimental results are of a nature such that we believe that the cell potentials we measured are valid, and that the electrical measurements we are reporting here are a faithful representation of the intrinsic character of the electrolytic reduction of Zn from ZnO.

RESULTS AND DISCUSSION

We did many experiments which had to be aborted because of apparatus failures. These were usually learning experiences and are described elsewhere.[26] In this section, we first present a few examples taken from the many experiments we did to illustrate some of our more general observations. Then we present a summary figure which combines the results we believe to be of archival interest.

Example experimental observations.

In a typical experiment we used a mixture of AlF_3 with NaF as the solvent, varying their molar ratios so as to control the melting point and the vapor pressure. We used the two eutectic mixtures of Fig. 2 in different experiments to achieve different volatilities.

the reactor configuration.[26]

Figure 5 shows a cell in the receiver-cavity. The cavity is enclosed on the incident-solar-flux side by a Pyrex window, a hemispherical dome, cut from a twelve liter round bottom flask, flanged and ground to a flat surface to mate well with the metal outer face-plate of the receiver. It was spring loaded against the face plate. Dow Corning High Vacuum Grease was used as a sealant.

The receiver itself contained two chambers. The forward chamber achieved temperatures as high as 2000K in the present study. It was insulated with a 2.5mm thick zirconia felt cloth, Zircar Products, Inc., ZYF-100, made of 4-5micron diameter yttria-stabilized zirconia fibers. We formed the insulating layer by wrapping the felt around a mandrel. The aperture was formed by wrapping the felt, in varying widths, between two cones.

The chamber which housed the electrolytic cell was insulated with Fiberfrax, an alumina-silica fibrous felt whose continuous use limit is 1530K. The back insulating plug was made of continuously wrapped Fiberfrax felt, 3.5 cm wide, backed by and glued to a rigid Fiberfrax board 2.5cm thick. The reactor shell was a 46cm long, 1cm thick, 31cm diameter 6061-T6 aluminum pipe, welded to 1.6cm thick grooved-for-O-ring aluminum flanges 40cm in diameter. The flanges accommodated 12 bolt holes. The 35.6cm O-rings were made of Viton, a fluoroelastomer said to be useful to about 530 K.

The front and back plates were made of 1.9cm thick 2024-T351 Al bolted to the flanges with 1/4 inch stainless steel bolts. The front plate was an annulus with a 22 cm inner diameter.

The septum between the two inner chambers was a 1.5cm thick graphite disk through which six 3mm holes had been drilled. Its purpose was to help keep solvent vapors from depositing on the cool window, since reducing the clarity of the window would result in its very rapid heating and destruction. To assure that there would be no deposition of condensible materials on the window, we flowed argon through the indicated tube in the bottom of the receiver, through the steel plate which supports the crucible, into the front section of the reactor, and then through the holes in the graphite disk. Radiation from the graphite disk was the principle source of energy transfer to the cell.

The electrolytic cell, shown in detail in Fig. 6, was contained in a graphite case, the crucible. It contained three electrodes: a graphite cathode, where Zn was deposited, a platinum anode, where O_2 was deposited, and the crucible itself, which

Figure 9 shows a plot of the variation of current with voltage in an experiment which made use of the less volatile, 13 mole% AlF_3 eutectic. The temperature was 1200K. The melting point of the solvent was 1161K; the boiling point of Zn is 1180K. We used a graphite crucible as the cathode and a graphite anode.

The zero-current potential in this experiment was 0.4 volt. For formation of CO at the anode, the standard potential is 0.014 volt; for the formation of CO_2 it is 0.118 volt. The overvoltage in this experiment is thus about 0.4 volt if the anode reaction yields CO and 0.3 volt if it yields CO_2. Experience from the aluminum industry suggests that typically overvoltages on graphite anodes are of the order 0.5 volt.

The experiment was straightforward to about 1.2 volts; although the second-to-second precision was not great, as is evident from the scatter of the individual data points, the current varied linearly with the voltage, and the result is a satisfactory plot of the current's variation with the applied voltage. At higher voltages the plot became much more erratic. The apparent resistance of the cell, the reciprocal of the slope, also abruptly became higher; when this happened, voltages as high as 8 volts, not shown in Fig. 9, sometimes produced currents as low as 1 ampere. Reducing the voltage to zero permitted the cell to recover and returned it to its normal state of behavior.

This sort of pathological behavior was typical of experiments in which we used graphitic anodes at high decomposition rates. We attribute it to the formation of an insulating layer of CO or CO_2 at the anode in a situation which is not unlike the abrupt decrease in heat transfer associated with a transition from nucleate boiling to film boiling heat transfer.

Figure 10 shows the results of a similar experiment conducted with a graphite crucible and graphite electrodes at 1073K. The lower melting eutectic of Fig. 2 was the solvent. The result clearly illustrates the anode effect associated with the transition from nucleate to film gas formation, starting at about 3.5 volts. At this temperature, the standard electrode potential for the formation of O_2 at the anode is 0.3 volt.

It was characteristic of many runs in which we used the graphite crucible that yields of Zn were higher than one would expect from the integrated time vs. current curves. The result was not surprising, since ZnO can be reduced by carbon at high temperatures and low Zn activities (partial pressures), in the range in which we worked. Although our electrochemical observations were reasonable, it was disconcerting to have to make our measurements with such a distraction. We therefore tried to served as the reference electrode against which the cathode and anode potentials were measured. The anode was surrounded by a graphite shroud which was electrically insulated from the anode and the crucible by BN rings. The shroud kept the product vapors from mixing and recombining. We attached the boron nitride ring separating the anode from the shroud to the anode by sandwiching it between two pieces of graphite which, in turn, were held together by the two halves of the threaded Monel connector. The two sheet metal strips shown attached to the shroud and bent over top of the BN ring permitted the shroud to be raised from the melt along with the anode. The cathode was also electrically insulated from the crucible by the boron nitride ring shown in the figure.

During electrolysis, O_2 formed at the anode flows through the Monel connector, into the graphite anode tube and thence to the atmosphere. Zinc formed at the cathode is swept by the argon through the Monel connector, into the graphite cathode tube and thence to the pyrex condenser and Fiberglas filter, shown in Fig. 5, which collect the zinc.

The connection between the cell and the condenser was made of graded glass. The part deepest inside the reactor was made of quartz, which was graded to Pyrex, where it joined the Pyrex condenser. The filter holder, shown in Fig. 5, was machined of aluminum plate. A fine copper screen supported the filter. The condenser and filter also collected solvent vapor which was being swept out by the argon.

Figure 7 shows the arrangement of the electrical measurement system. The anode is platinum; the cathode is graphite. A third electrode is the graphite crucible itself. The anode and cathode potentials were measured against that of the crucible. Their sum gives the cell potential. The total cell potential, which included the ohmic drop, was also measured across the working electrodes for comparison. Our data logger, a Doric Digitrend 235, can measure voltages to 2V. To measure and record higher voltages we used the two-resister voltage dividers shown in the figure. The voltage drop across one of the resistors, about one-third of the actual voltage drop, was measured. The desired voltage was calculated internally by the data reduction system. We determined the current by measuring the voltage drop across the shunt resistor shown. Each mV coresponded to one ampere.

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We used an IBM personal computer for reducing and manipumitigate the problem by plating the inside of the graphite casing with BN.

An example electrochemical measurement we made in a boron nitride lined crucible is shown in Fig. 11. The solvent was $0.13AlF_3$-$0.87NaF$; the temperature was 1200K. We used a Pt anode and a graphite cathode. We recovered 93% of the expected Zn and measured a decomposition potential of 1.28 volts, which is to be compared with the standard potential for the decomposition of ZnO at this temperature, 1.15 volts. In this experiment we also observed, at low voltages, the phenomenon of underpotential-deposition, UPD, which is observed with other systems, as well, but for which we do not, as yet, have a satisfactory explanation. The phenomenon appears in the figures as a flow of current at emfs below the decomposition potential obtained by linear extrapolation of the voltage-current curve.

BN, in spite of the fine result shown in Fig. 11, turned out to be an unreliable crucible liner. An attempt to use it at 1300K, Fig. 12, resulted in the destruction of the coating and a 286% yield of Zn. ZnO evidently reacted with the unprotected graphite. Nevertheless, the voltage-current curve seems to be satisfactory. After having been corrected for UPD it suggests a decomposition potential of 1.2 volts.

Figure 13 shows the individual electrode potentials, with reference to the graphite crucible, of a platinum anode and graphite cathode, as well as the overall potential required to produce a given current flow. The solvent is $0.13AlF_3$-$0.87NaF$ and the temperature is 1200K. It is noteworthy that virtually all of the voltage drop is experienced across the anode, where the more complex gas is being produced.

The behavior of ZnO in $0.33ZnF_2$-$0.67NaF$ is electrochemically little different than it is in the cryolites, Fig. 14. This experiment was done in a graphite crucible using a platinum anode and graphite cathode at 1000K. Here, too, there was a small voltage drop across the cathode. Most of the decomposition potential was across the anode.

Because of the erratic nature of the Zn yields caused by the direct reaction of ZnO with graphite we felt it appropriate to compare the results of two nominally identical experiments in one of which there was no ZnO. The solvent was $0.33ZnF_2$-$0.67NaF$. We used a platinum anode and a graphite cathode. The temperature was 1100K. The results are shown in Fig. 15. In the absence of ZnO the decomposition potential was 2.4 volts; in its presence, it was about 1.25 volts. The experiment thus suggests that we were, indeed, measuring the decomposition potential of ZnO, and that the activity of the ZnO in the solution was that of solid ZnO.

lating the data and for storing it on floppy discs and a Bausch and Lomb, Houston Instruments eight pen plotter for plotting the results.

Procedure.

The first step in preparing for an experiment was to load the crucible with solvent and ZnO. The solvent was either freshly prepared, or the recrushed melt from a previous run was used. Enough ZnO was added to insure that the melt would remain saturated. The chemical potential of ZnO in solution was therefore the same as that of the solid. The crucible was then covered, and the electrodes were inserted. Then the crucible was placed in the receiver, the anode and cathode tubes were threaded onto the electrodes, the crucible was connected to the steel plate by nichrome wire, and one thermocouple was inserted into the crucible base. Finally, the insulating plug was inserted and the back plate of the receiver was bolted on.

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Decomposition potential of ZnO in the range 600-1400K.

Figure 16 summarizes the decomposition potentials we observed with ZnO over a temperature range 600-1400K. We used a variety of solvents. Over the lower part of the range, from below the melting point of Zn to the melting point of the $0.33ZnF_2$-$0.67NaF$ eutectic, we used NaOH. In the range 1000-1200K, to just above the boiling point of Zn, we used the $0.33ZnF_2$-$0.67NaF$ eutectic, and in the range 1200-1400K we used $0.13AlF_3$-$0.87NaF$. In all of these experiments the cathode was graphite and the anode was platinum. The data points are the experimentally determined decomposition potentials, which were obtained by linear extrapolation of the voltage-current curves to zero current, ignoring the underpotential deposition. The solid line is the theoretical standard state decomposition potential for the production of molecular O_2 and elementary Zn in its standard state at the electrolysis temperature.

The overvoltage decreases from about 0.8 volt at 600K to about 0.2 volt at the boiling point of Zn, near 1200K. At higher temperatures, the decomposition potential apparently rises dramatically with temperature.

We attribute the remarkable increase in the electrode potential observed at 1300 and 1400K to the fact that at these temperatures the change in gibbs function for the reduction of ZnO by graphite is such as to permit its direct reduction at the cathode, in addition to its electrolytic reduction, resulting in a build-up of CO at the cathode, as well as at the anode. At 1400K the reaction is apparently much faster than it is at 1300K.

At 1200K the direct reduction may occur at the graphite walls, but apparently not yet at the cathode, where the reaction, ZnO + C ---> Zn + CO would be diminished by the presence of electrolytically produced Zn. This conjecture is supported by the results shown in Fig. 17, which shows the individual electrode potentials correlating to the decomposition potentials of Fig. 16.

It may also be noteworthy that in the lower temperature range, in NaOH, the anode potential was lower than that of the cathode, and that there was an apparent reversal of the electrode reactions' role in the kinetics of the process. We were unable to recover elemental Zn from the experiments which took place in NaOH, unless we made use of a nickel cathode under conditions which resulted in the formation of a nickel-zinc alloy, a fact that may perhaps be attributed to the amphoteric nature of Zn in its reactions with NaOH. Such an effect might also account for

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RESULTS AND DISCUSSION

We did many experiments which had to be aborted because of apparatus failures. These were usually learning experiences and are described elsewhere.[26] In this section, we first present a few examples taken from the many experiments we did to illustrate some of our more general observations. Then we present a summary figure which combines the results we believe to be of archival interest.

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the apparent change in mechanism of the electrolysis suggested by the reversal. If such an attribution is valid, then it appears that the effect is obtained only at lower temperatures, and that, at higher temperatures, such interactions become less important.

We have no clear explanation for the underpotential deposition current observed in these experiments. One rationale might be that the oxygen activity at the anode is reduced to substantially less than one atmosphere unless electrolysis is taking place fast enough to cause bubbles to form against an external pressure of one atmosphere, by some sort of interaction of the cell material with the platinum itself.

SUMMARY AND CONCLUSIONS

We have measured in a solar furnace and reported the decomposition potentials of ZnO in a variety of electrolytes in the temperature range 600-1400K. As thermodynamics predicts, the decomposition potential of ZnO decreases as the temperature increases. The overvoltages decrease as temperature increases, as well. From 1200 to 1400K, the direct reaction of the graphite cathode with ZnO in the melt so dominates the process that the decomposition potential apparently increases. The increase is not real, however; it results from the formation of a gas barrier of oxides of carbon produced by the direct reaction of the cathode with ZnO in the melt.

During the course of the present research we learned a great deal about the kinds of problems one can encounter and gained experience which should be of interest to those who contemplate doing very high temperature electrochemical studies in solar furnaces. We made many false starts but eventually learned how to do meaningful experiments. Throughout the present study we were consoled by the knowledge that we were doing pioneering research. In such a situation good judgement often comes with experience, and experience comes with bad judgement. Many of the problems we encountered are described, somewhat chronologically, for the mischievous, elsewhere.[26] This summary of our conclusions about experimental techniques and materials should give others the benefit of our experience and help them avoid some of the consequences of bad judgement.

Electrode Materials

Graphite is an excellent material for either electrode. It held up to all our solvents at all temperatures. Threaded connections of steel or nichrome to the graphite made good electrical contact and were structurally adequate.

Pt was also an excellent electrode material, particularly for the anode. We did not use it as a cathode to avoid zinc's alloying with it. It survived exposure to all the solvents over the temperature range over which we worked, even NaOH at 1100 K, although it has been reported that significant corrosion occurred in molten NaOH above 873K. It was attacked, however at high voltages in fluoride melts with little or no oxide present. Fluorine liberated at the anode apparently corrodes Pt quickly.

Ni was not suitable in cryolite-type solvents. It apparently undergoes dissolution as a consequence of electrode reactions. As an anode, it must be used with caution since it could react to form an oxide. As a cathode in NaOH it permitted us to collect Zn by alloying with it, thus preventing the destructive reaction of Zn with NaOH.

Mo cannot be used as an anode since it readily forms volatile oxides. We made one attempt to use it as a cathode. It failed. It simply disappeared, possibly as a result either of oxidation by traces of O_2 or from alloying with zinc and melting.

Electrical Insulators

BN, being a good heat conductor was a very stable insulator which did not seem to be very subject to damage by thermal shock. As long as we kept it from direct contact with the molten salts, it worked well. It is brittle, but care in machining and handling reward the experimentalist with component parts that are useful and fairly long-lived. It deteriorated quickly when it came into contact with the electrolyte itself.

In a few experiments, we tried alumina/silica board for electrical insulation. In the shapes we used it fell apart too easily. Electrically, it was adequate. Perhaps a densified form would make it more useful.

Solvents

NaOH is liquid over a wide range of temperatures and cheap. However, Zn produced in its presence must be collected as an alloy.

The eutectic $0.33ZnF_2$-$0.67NaF$ may be a good low temperature range solvent for use with ZnO. More studies should be done to determine solubilities, and a range of ZnF_2-NaF compositions should also be investigated. Temperatures above 1100K are attracmitigate the problem by plating the inside of the graphite casing with BN.

An example electrochemical measurement we made in a boron nitride lined crucible is shown in Fig. 11. The solvent was which condense on the inside of the dome absorb energy, causing it to get hot, producing thermal stresses or softening which can lead to its failure.

Acknowledgements- We thank The Office of Naval Research and The Northern States Power Company for their generous support of this research. H. Scherrer created the software for displaying, logging, recording, and plotting the data, R. Palumbo, T. Kappauf, and J. Murray were especially helpful with some of the experiments, and we profited from helpful discussions with M. Levy of the Weitzmann Institute of Science.

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13. J. Thonstad, Model of Diffusion Layer for Cathodic Deposition

the apparent change in mechanism of the electrolysis suggested by the reversal. If such an attribution is valid, then it appears that the effect is obtained only at lower temperatures, and that, at higher temperatures, such interactions become less important.

We have no clear explanation for the underpotential deposition current observed in these experiments. One rationale might be that the oxygen activity at the anode is reduced to substantially less than one atmosphere unless electrolysis is taking place fast enough to cause bubbles to form against an external pressure of one atmosphere, by some sort of interaction of the cell material with the platinum itself.

SUMMARY AND CONCLUSIONS

We have measured in a solar furnace and reported the decomposition potentials of ZnO in a variety of electrolytes in the temperature range 600-1400K. As thermodynamics predicts, the decomposition potential of ZnO decreases as the temperature increases. The overvoltages decrease as temperature increases, as well. From 1200 to 1400K, the direct reaction of the graphite cathode with ZnO in the melt so dominates the process that the decomposition potential apparently increases. The increase is not real, however; it results from the formation of a gas barrier of oxides of carbon produced by the direct reaction of the cathode with ZnO in the melt.

During the course of the present research we learned a great deal about the kinds of problems one can encounter and gained experience which should be of interest to those who contemplate doing very high temperature electrochemical studies in solar furnaces. We made many false starts but eventually learned how to do meaningful experiments. Throughout the present study we were consoled by the knowledge that we were doing pioneering research. In such a situation good judgement often comes with experience, and experience comes with bad judgement. Many of the problems we encountered are described, somewhat chronologically, for the mischievous, elsewhere.[26] This summary of our conclusions about experimental techniques and materials should give others the benefit of our experience and help them avoid some of the consequences of bad judgement.

Electrode Materials

Graphite is an excellent material for either electrode. It held up to all our solvents at all temperatures. Threaded connections of steel or nichrome to the graphite made good electrical contact and were structurally adequate.

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Pt was also an excellent electrode material, particularly for the anode. We did not use it as a cathode to avoid zinc's alloying with it. It survived exposure to all the solvents over the temperature range over which we worked, even NaOH at 1100 K, although it has been reported that significant corrosion occurred in molten NaOH above 873K. It was attacked, however at high voltages in fluoride melts with little or no oxide present. Fluorine liberated at the anode apparently corrodes Pt quickly.

Ni was not suitable in cryolite-type solvents. It apparently undergoes dissolution as a consequence of electrode reactions. As an anode, it must be used with caution since it could react to form an oxide. As a cathode in NaOH it permitted us to collect Zn by alloying with it, thus preventing the destructive reaction of Zn with NaOH.

Mo cannot be used as an anode since it readily forms volatile oxides. We made one attempt to use it as a cathode. It failed. It simply disappeared, possibly as a result either of oxidation by traces of O_2 or from alloying with zinc and melting.

Electrical Insulators

BN, being a good heat conductor was a very stable insulator which did not seem to be very subject to damage by thermal shock. As long as we kept it from direct contact with the molten salts, it worked well. It is brittle, but care in machining and handling reward the experimentalist with component parts that are useful and fairly long-lived. It deteriorated quickly when it came into contact with the electrolyte itself.

In a few experiments, we tried alumina/silica board for electrical insulation. In the shapes we used it fell apart too easily. Electrically, it was adequate. Perhaps a densified form would make it more useful.

Solvents

NaOH is liquid over a wide range of temperatures and cheap. However, Zn produced in its presence must be collected as an alloy.

The eutectic $0.33ZnF_2$-$0.67NaF$ may be a good low temperature range solvent for use with ZnO. More studies should be done to determine solubilities, and a range of ZnF_2-NaF compositions should also be investigated. Temperatures above 1100K are attrac-

FIGURE CAPTIONS

Fig. 1. Phase diagram for ZnO on temperature-pressure coordinates (Ref. 1.)

Fig. 2. Phase diagram for the NaF-AlF_3 system (Ref. 15). The temperature is in ^{o}C.

Fig. 3. Phase diagram for the NaF-ZnF_2 system (Ref. 18). T is in ^{o}C.

Fig. 4. An exemplary current vs. voltage curve. E_{th} is the theoretical decomposition potential, E_d is the actual decomposition potential, and I_L is the limiting current.

Fig. 5. The electrolytic cell assembly within the cavity receiver. The chamber on the left is the cell cavity. It is separated from the chamber on the right, in which the direct radiation from the sun is collected by the preforated graphite wall through which Ar flows. The flow of Ar serves two purposes: It keeps the window clean and cool by preventing the backflow of condensible volatiles from the cell, and it sweeps Zn vapor from the cell to the condenser-filter, where it is collected.

Fig. 6. The final configuration of the electrolysis cell. Oxygen liberated at the Pt anode bubbled up through the graphite shroud through its chimney to the exterior. Zinc vapor from the remaining vapor space in the cell was swept through the cathode chimney by the flow of Ar, into the condenser-filter.

Fig. 7. Schematic diagram of the electrical measurements system.

Fig. 8. Computer print out of the insolation and the concommitent temperature histories of the receiver and crucible temperatures. It is evident that even though the insolation was noisy and variable because of the passage of a thin layer of clouds, manipulation of the furnace doors and the thermal inertia of the furnace itself made good temperature control possible.

Fig. 9. Variation of current with applied voltage at 1220K. The solvent is $0.13AlF_3$-0.87NaF. The anode was graphite. A graphite crucible served as the cell casing as well as a cathode. For the formation of CO at the anode, the standard electrode potential is 0.014V.

tive inasmuch as the collection of zinc vapor appears to be much easier than recovering liquid Zn.

The substance $0.13AlF_3$-$0.87NaF$ is a fairly well characterized solvent. It is similar to cryolite and easy to work with. It shrinks away from the crucible walls upon solidification. It dissolves enough ZnO to sustain electrolysis at high current densities and its vapors do not appear to corrode the boron nitride electrical insulation. Its high temperature range is attractive in that it permits electrolysis at satisfactorily low voltages.

Crucibles and Cell Casings

Graphite is an ideal material in many respects. It is easy to machine and to fabricate into component parts. In the present study, it furnished us with an excellent example of a situation in which the requirement for the use of electrical energy is decreased because of the decrease in the gibbs function with temperature associated with a positive entropy change of the reaction. As the temperature rose, the mechanism by which reduction was achieved in the presence of graphite gradually changed from one that was electrolytic to one that was predominantly direct reduction of the oxide by graphite. With many other oxides, however, direct reduction would be much more difficult or impossible to achieve, except at very reduced pressures. In such situations, graphite should be ideal for the fabrication of the cell components. That being so, although we briefly considered the possibility of using SiC or virteous graphite for cell casings, we did no experimental work with them.

Our experience with Ni anodes and one experiment we did using a Ni crucible as a cell casing suggests that it is too reactive with fluorine containing electrolytes to be used with them.

Pt held up well as an anode material, but our limited experience in using it in a situation in which it could come in contact with Zn suggests that it should not be used, except perhaps at very high temperatures, where the greater volatility of Zn might be expected to preclude alloy formation. We are continuing studies of such situations.

Quartz was quickly damaged in the fluoride melts, probably because of the presence of trace amounts of water.

A very important consideration in the conduct of the experiments was the cleanliness of the window. Solvent vapors and Zn

Fig. 10. Variation of current with applied voltage at 1073K. The solvent is $0.45AlF_3$-$0.55NaF$. The cell casing was a graphite crucible. Two separate graphite electrodes were used as anode and cathode. For the formation of CO at the anode, the standard electrode potential is 0.30V.

Fig. 11. Variation of current with applied voltage at 1200K. The solvent is $0.13AlF_3$-$0.87NaF$. The anode was platinum. The cathode was graphite. A graphite crucible lined with BN served as the cell casing. For the formation of O_2 at the anode, the standard electrode potential is 1.15V.

Fig. 12. Variation of current with applied voltage at 1300K. The solvent is $0.13AlF_3$-$0.87NaF$. The anode was platinum. The cathode was graphite. A graphite crucible initially lined with boron nitride served as the cell casing. For the formation of O_2 at the anode, the standard electrode potential is 1.05V.

Fig. 13. Variation of current with applied voltage at 1200K. The solvent is $0.13AlF_3$-$0.87NaF$. The anode was platinum. The cathode was graphite. A graphite crucible served as the cell casing. For the formation of O_2 at the anode, the standard electrode potential is 1.15V. The triangles give the cathode potential, the circles give the anode potential, and the squares give the cell potential.

Fig. 14. Variation of current with applied voltage at 1000K. The solvent was $0.33ZnF_2$-$0.67NaF$. The anode was platinum. The cathode was graphite. A graphite crucible served as the cell casing. For the formation of O_2 at the anode, the standard electrode potential is 1.28V. The triangles give the cathode potential, the circles give the anode potential, and the squares give the cell potential.

Fig. 15. Variation of current with applied voltage at 1100K. The solvent was $0.33ZnF_2$-$0.67NaF$. The anode was platinum. The cathode was graphite. A graphite crucible served as the cell casing. For the formation of O_2 at the anode, the standard electrode potential is 1.22V. The squares were obtained with no ZnO in the melt. The circles were obtained with the melt saturated with ZnO. If the points attributed to underpotential deposition are ignored, a zero-current potential of about 2.4 volts is suggested for the melt in which there was no added ZnO, and a zero-current potential of about 1.4 volts is suggested for the melt which was saturated with ZnO and in contact with the solid.

Fig. 16. Variation of the zero current decomposition potential of ZnO to Zn and O_2 with temperature using a platinum anode with a graphite cathode, in three solvents. From below the melting point of Zn to the melting point of the $0.33ZnF_2$-$0.67NaF$ eutectic, we

which condense on the inside of the dome absorb energy, causing it to get hot, producing thermal stresses or softening which can lead to its failure.

Acknowledgements- We thank The Office of Naval Research and The Northern States Power Company for their generous support of this research. H. Scherrer created the software for displaying, logging, recording, and plotting the data, R. Palumbo, T. Kappauf, and J. Murray were especially helpful with some of the experiments, and we profited from helpful discussions with M. Levy of the Weitzmann Institute of Science.

used NaOH as the solvent. In the range 1000-1200K, to just above the boiling point of Zn, we used the 0.33ZnF$_2$-0.67NaF eutectic, and in the range 1200-1400K we used 0.13AlF$_3$-0.87NaF. The solid lines are theoretical standard decomposition potentials.

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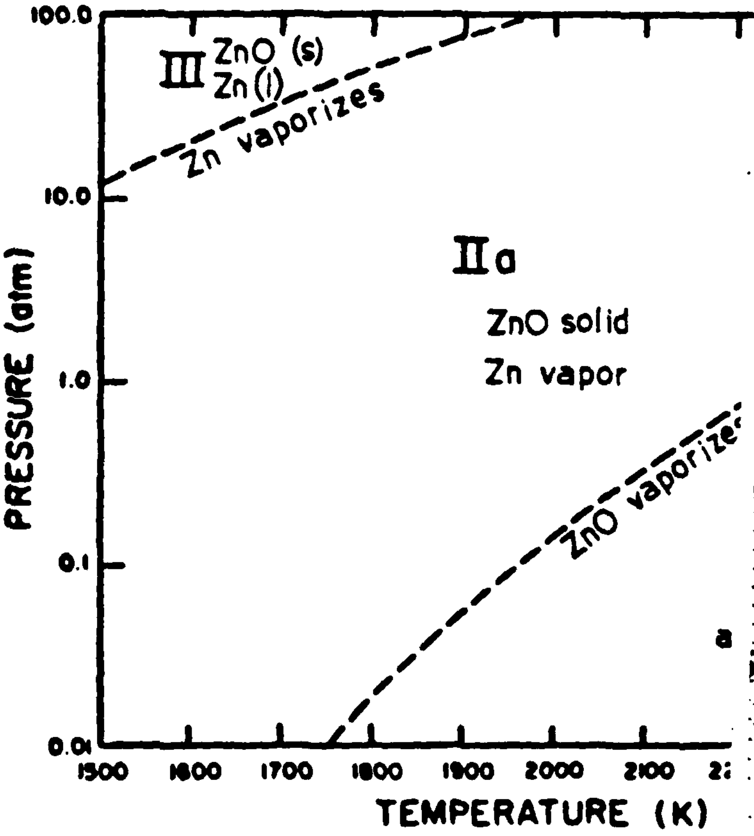
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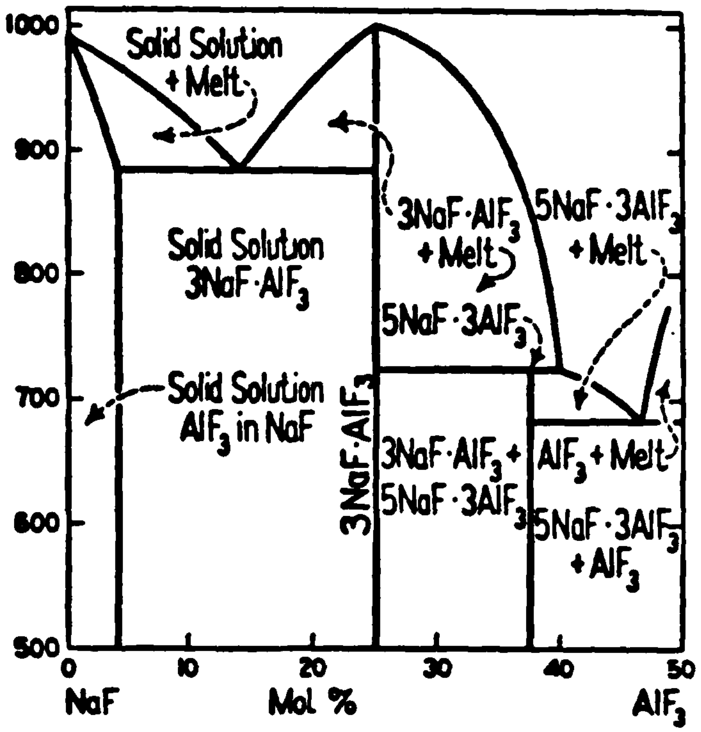

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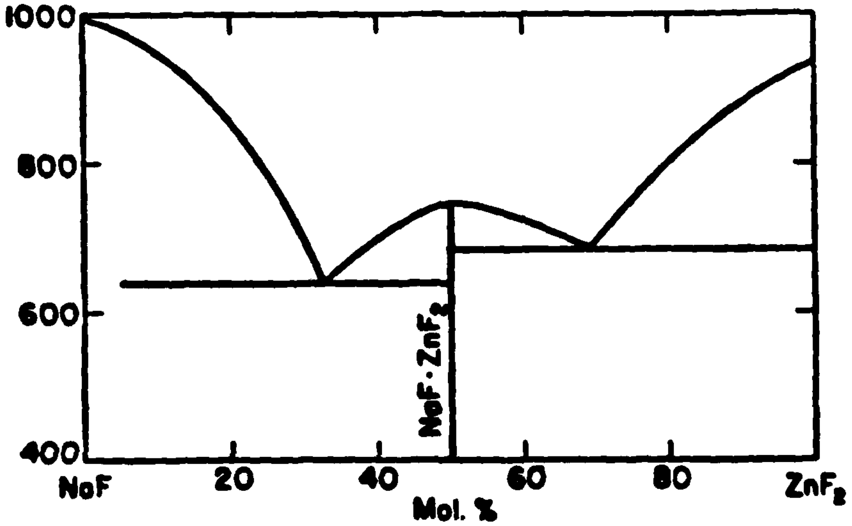

FLETCHER, FIGURE 3

FIGURE CAPTIONS

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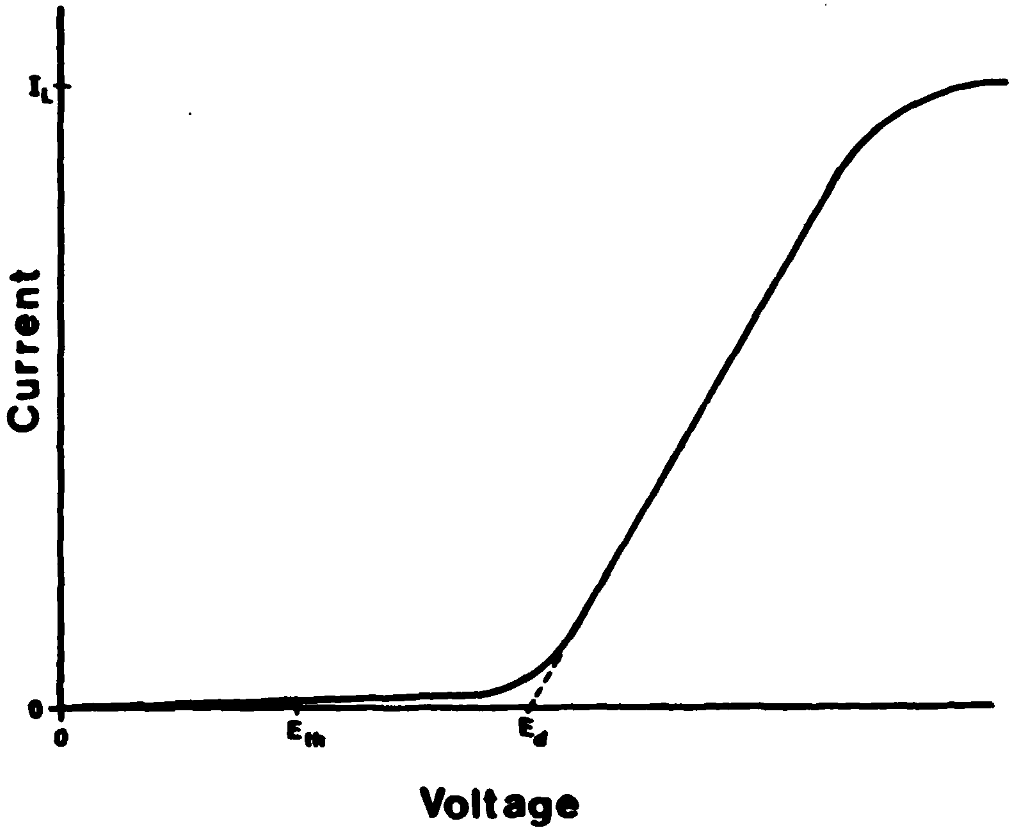

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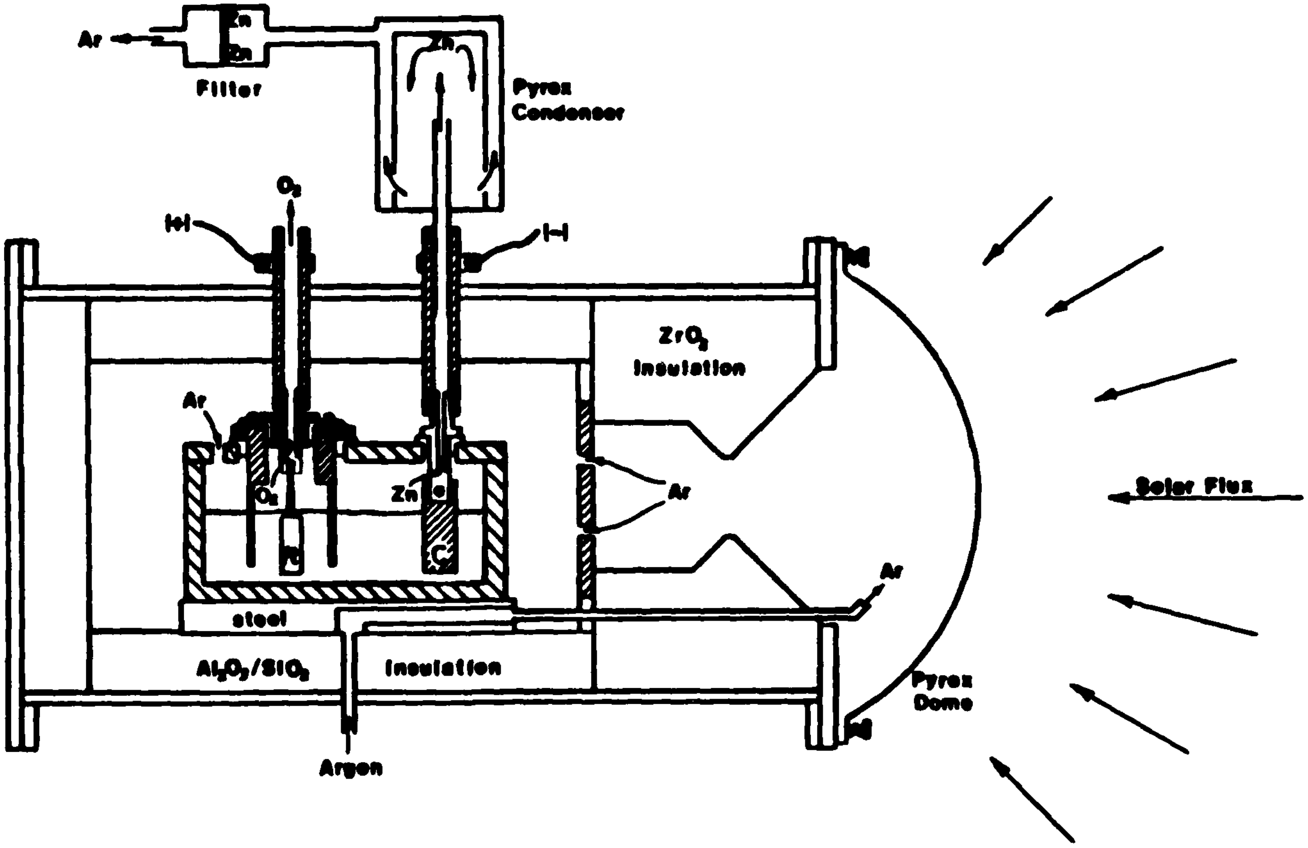

FLETCHER, FIGURE 5

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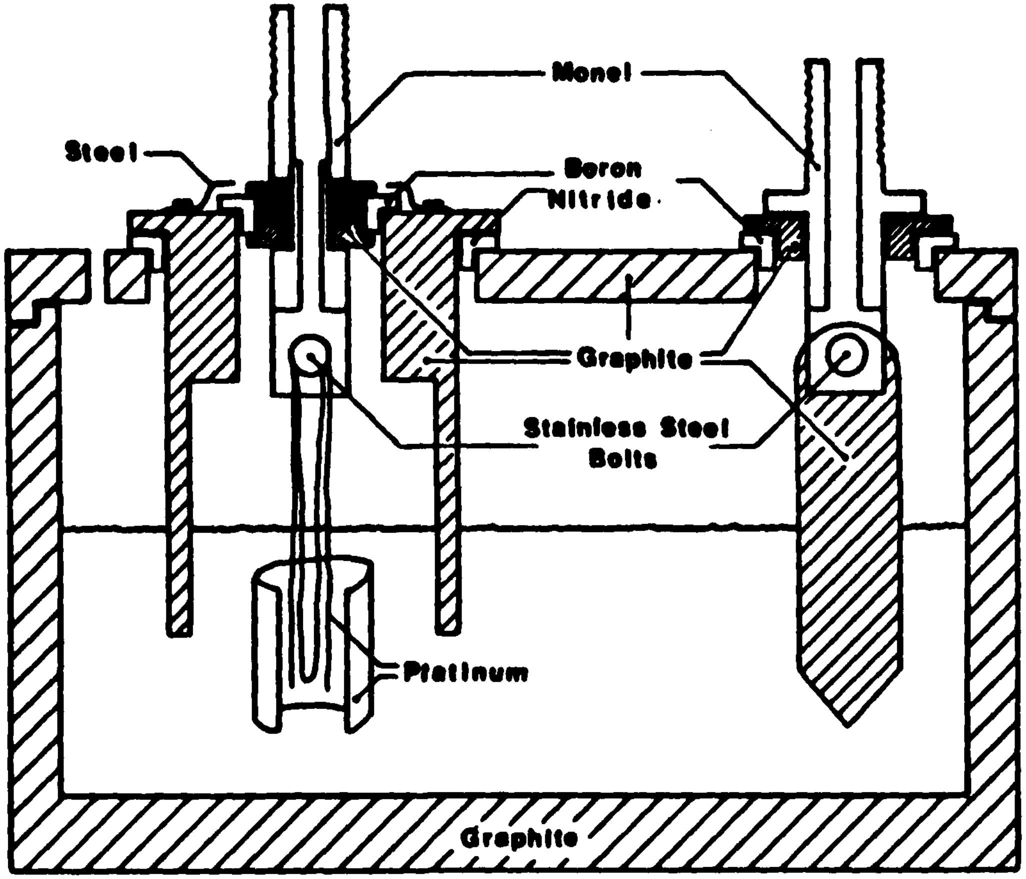

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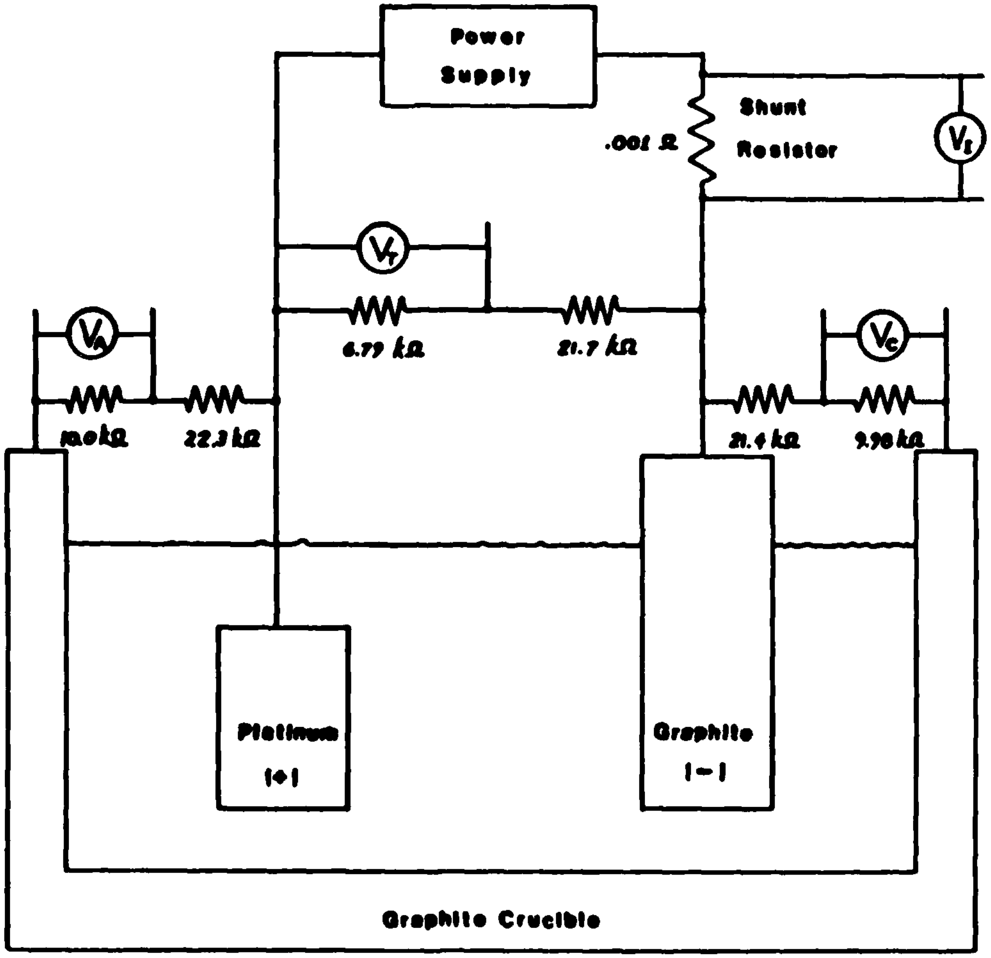

FLETCHER, FIGURE 7

used NaOH as the solvent. In the range 1000-1200K, to just above the boiling point of Zn, we used the 0.33ZnF$_2$-0.67NaF eutectic, and in the range 1200-1400K we used 0.13AlF$_3$-0.87NaF. The solid lines are theoretical standard decomposition potentials.

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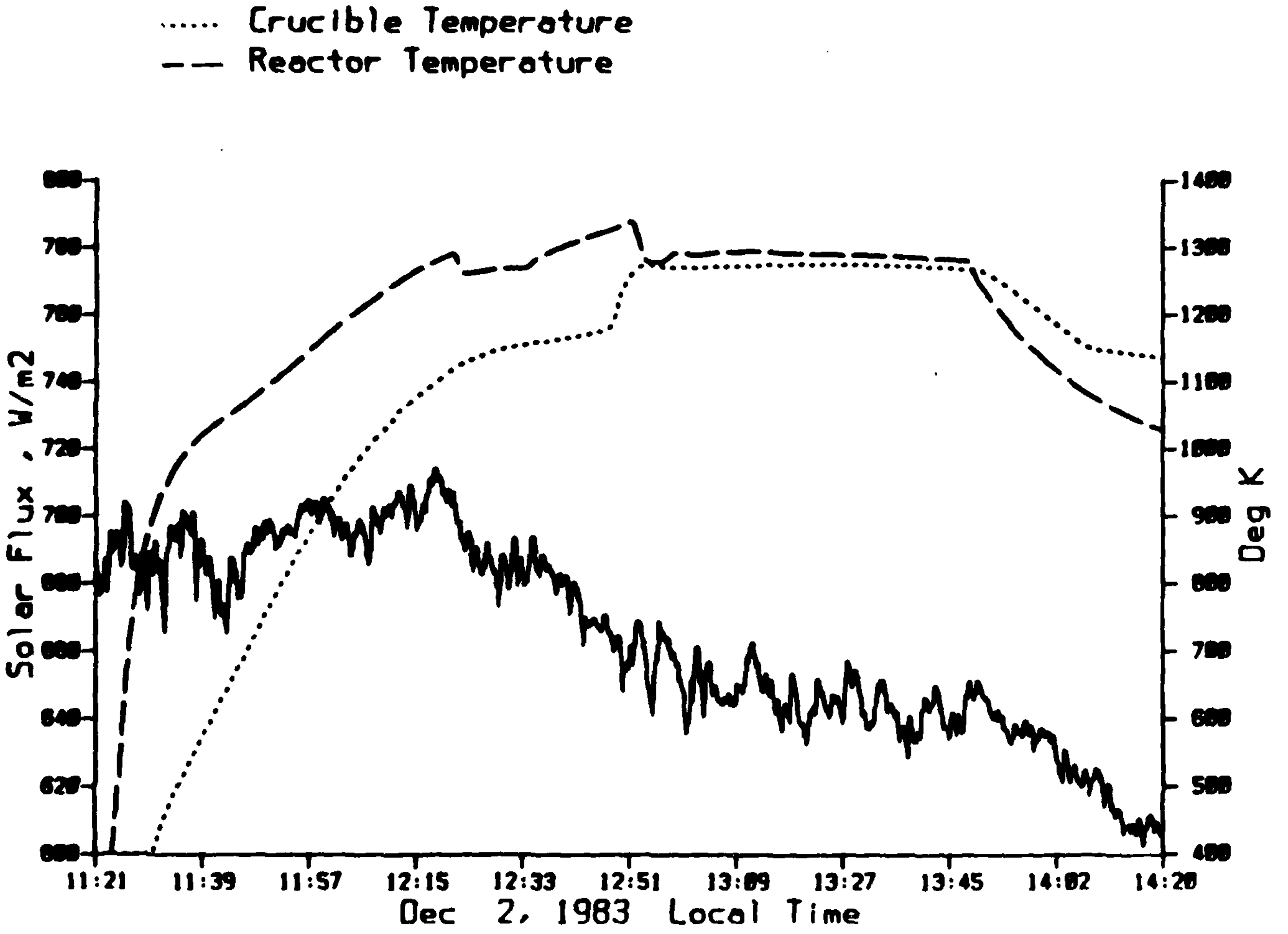

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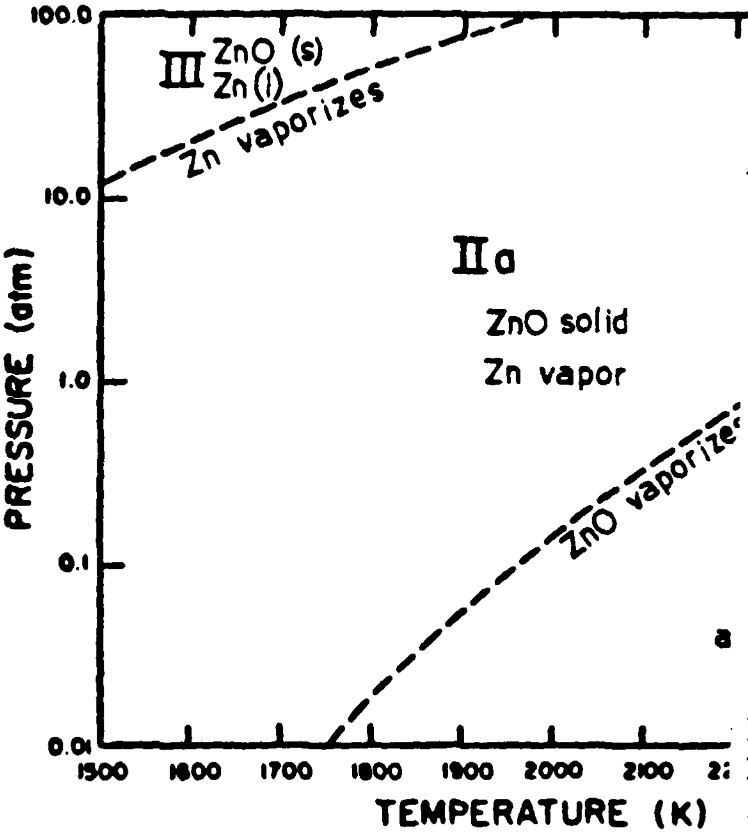
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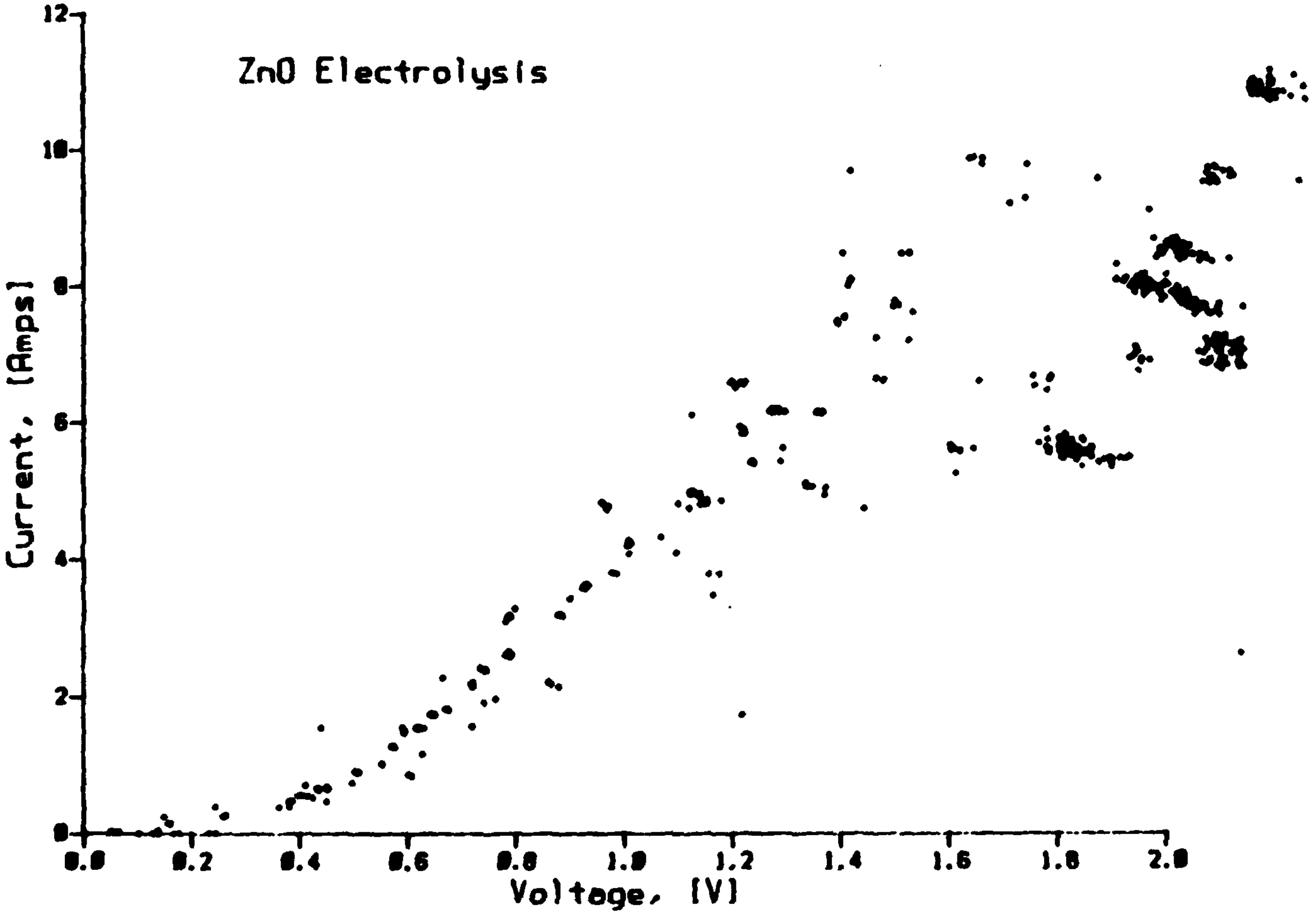

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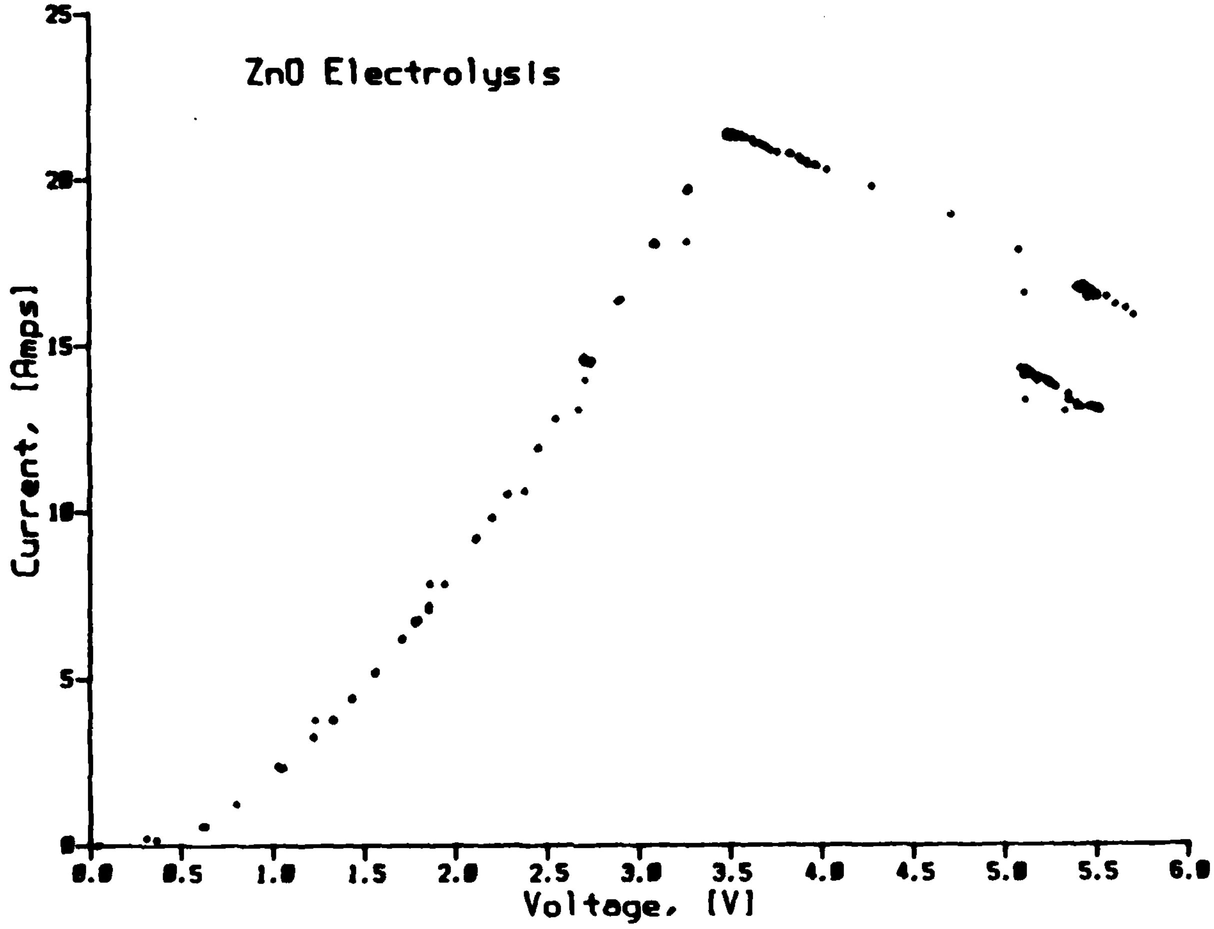

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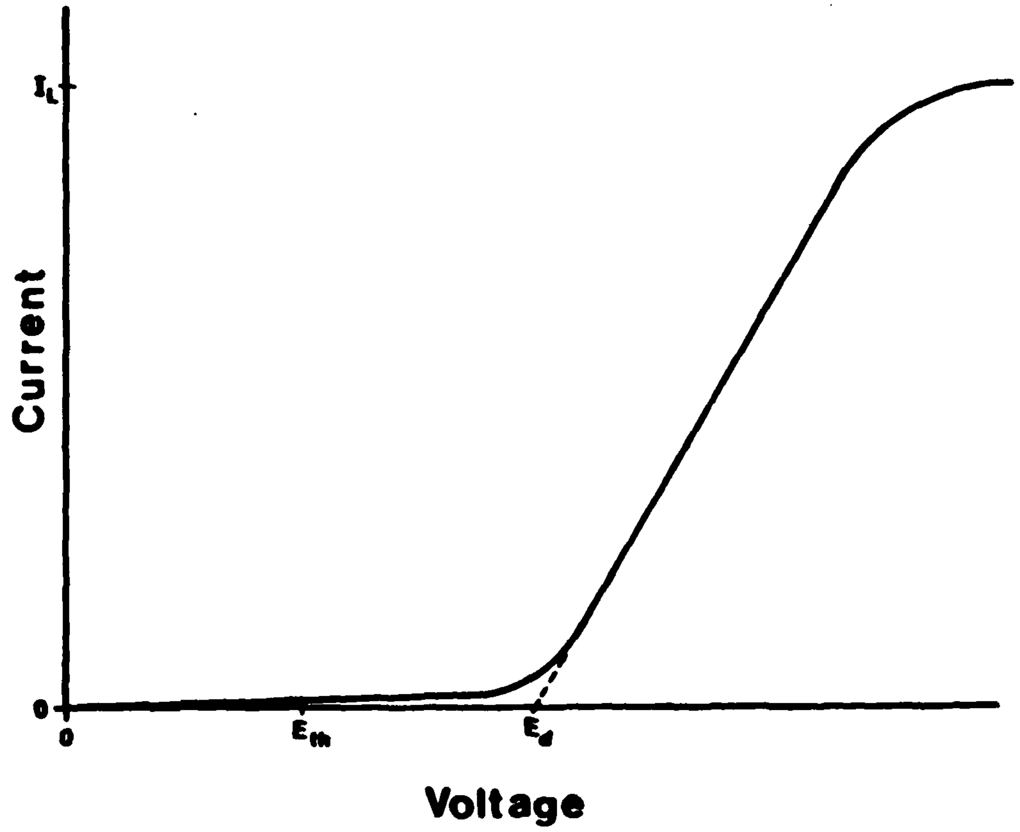

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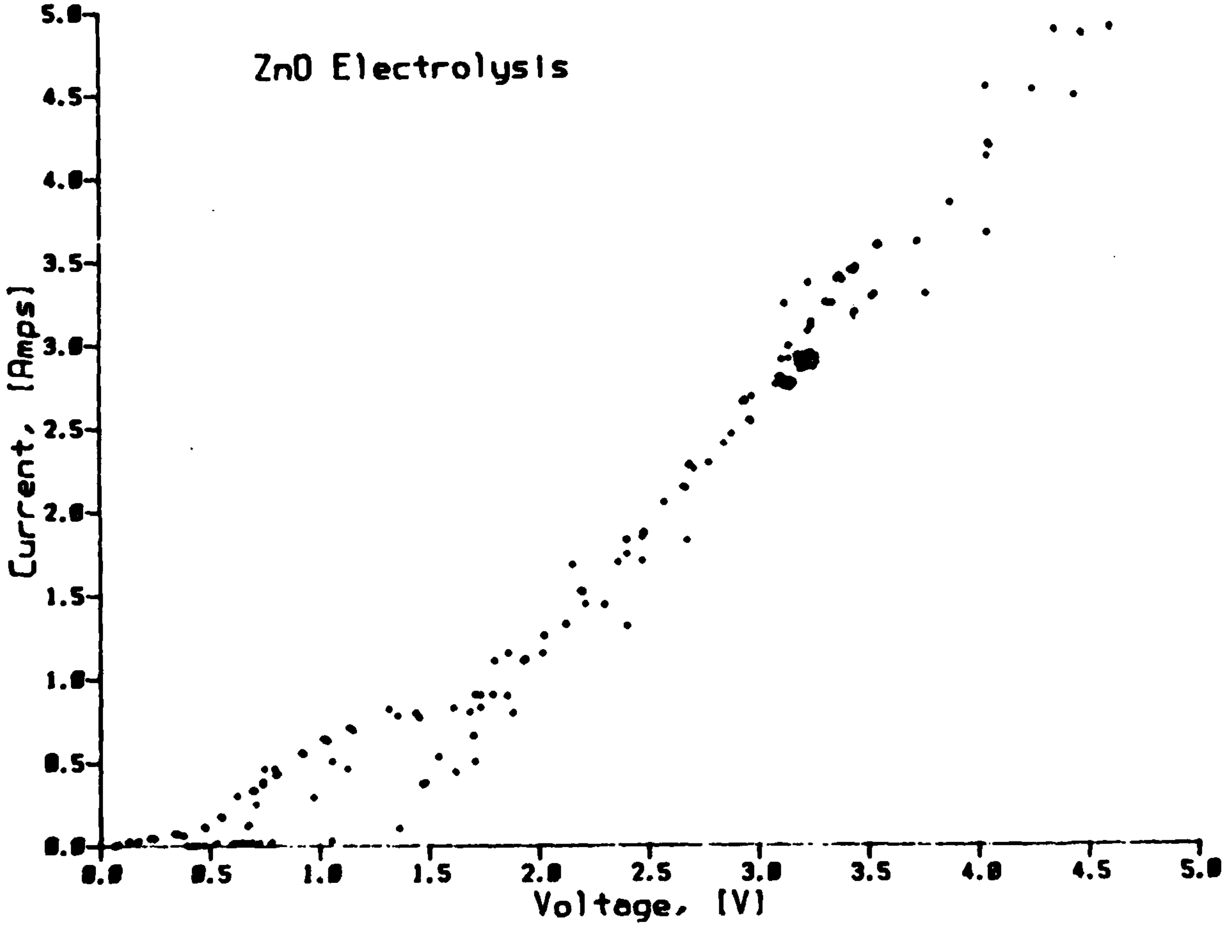

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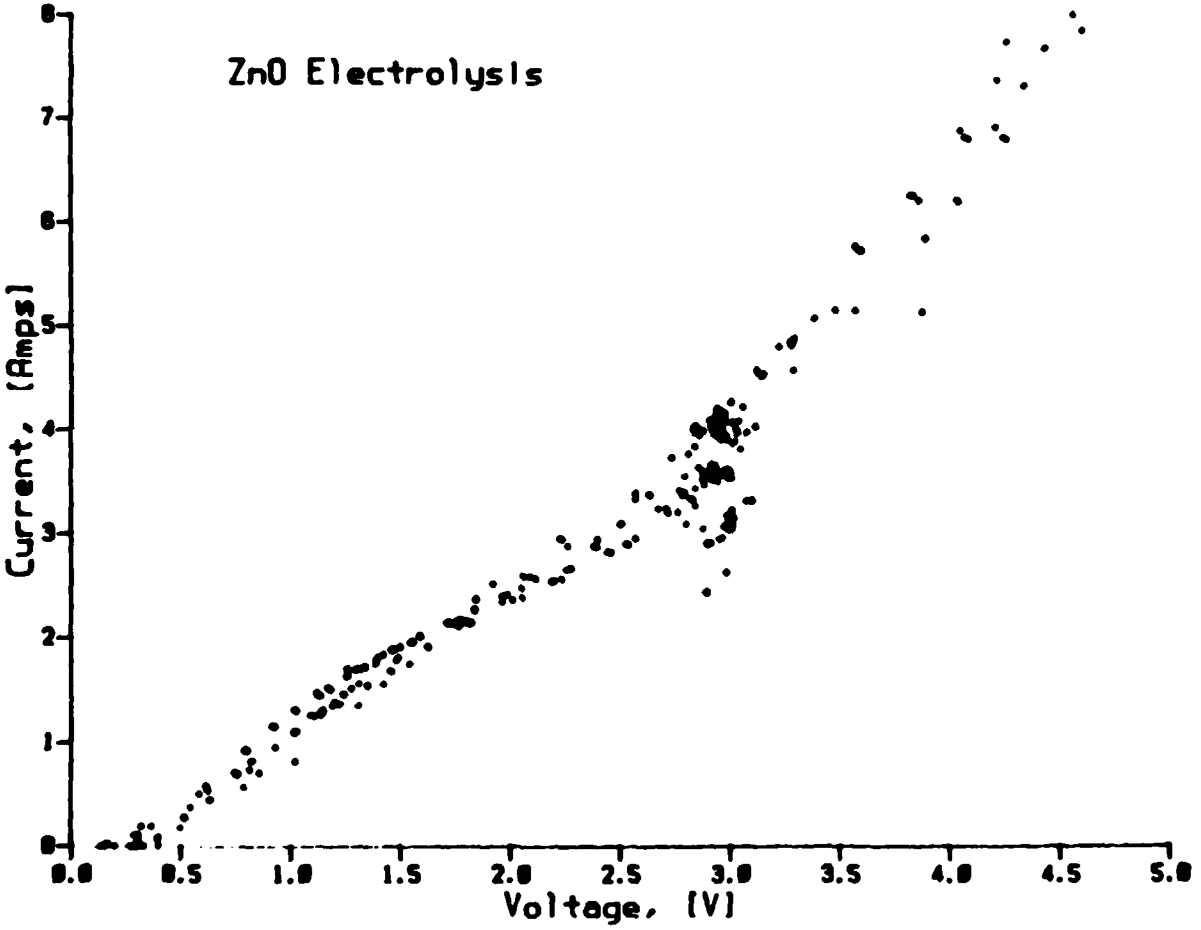
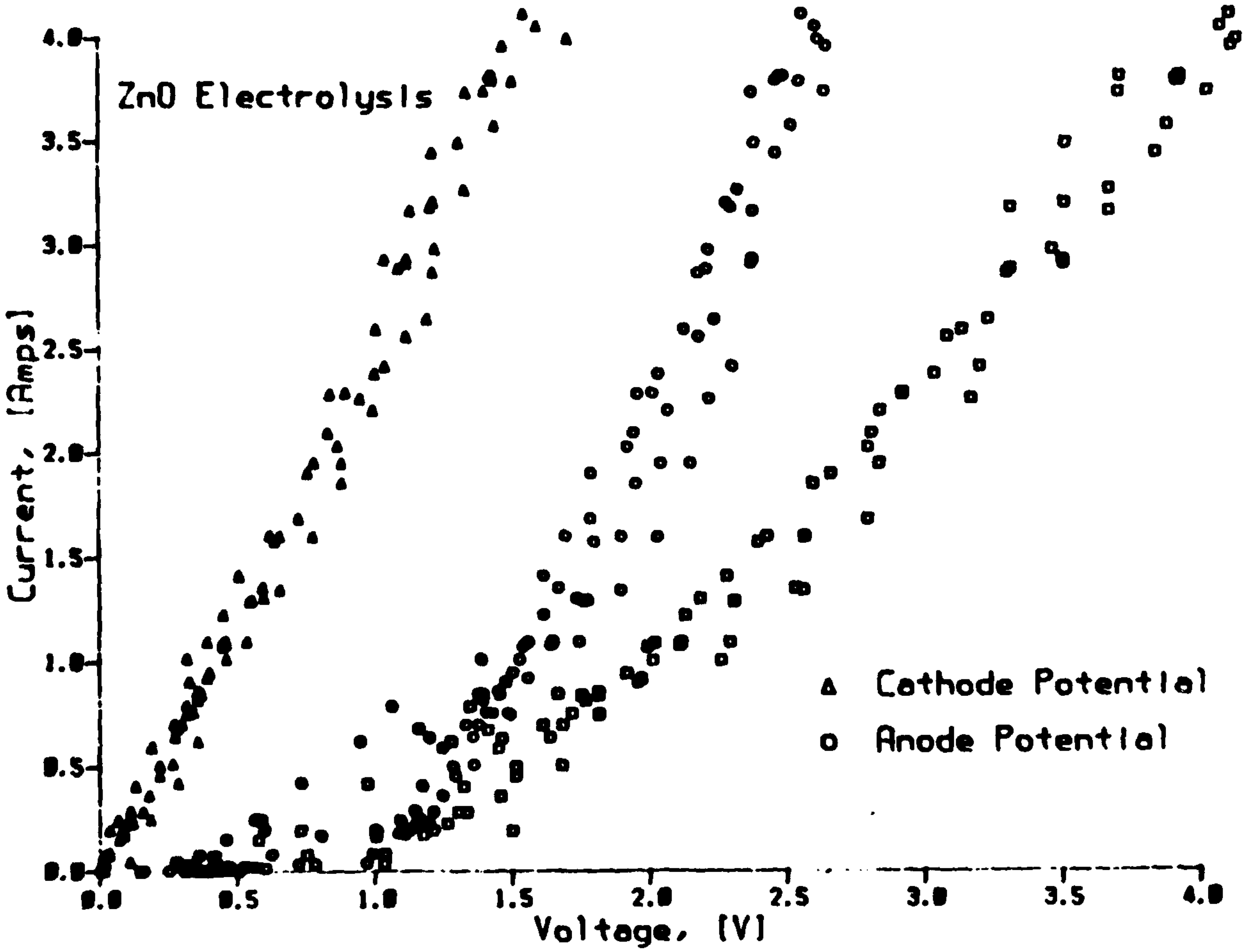
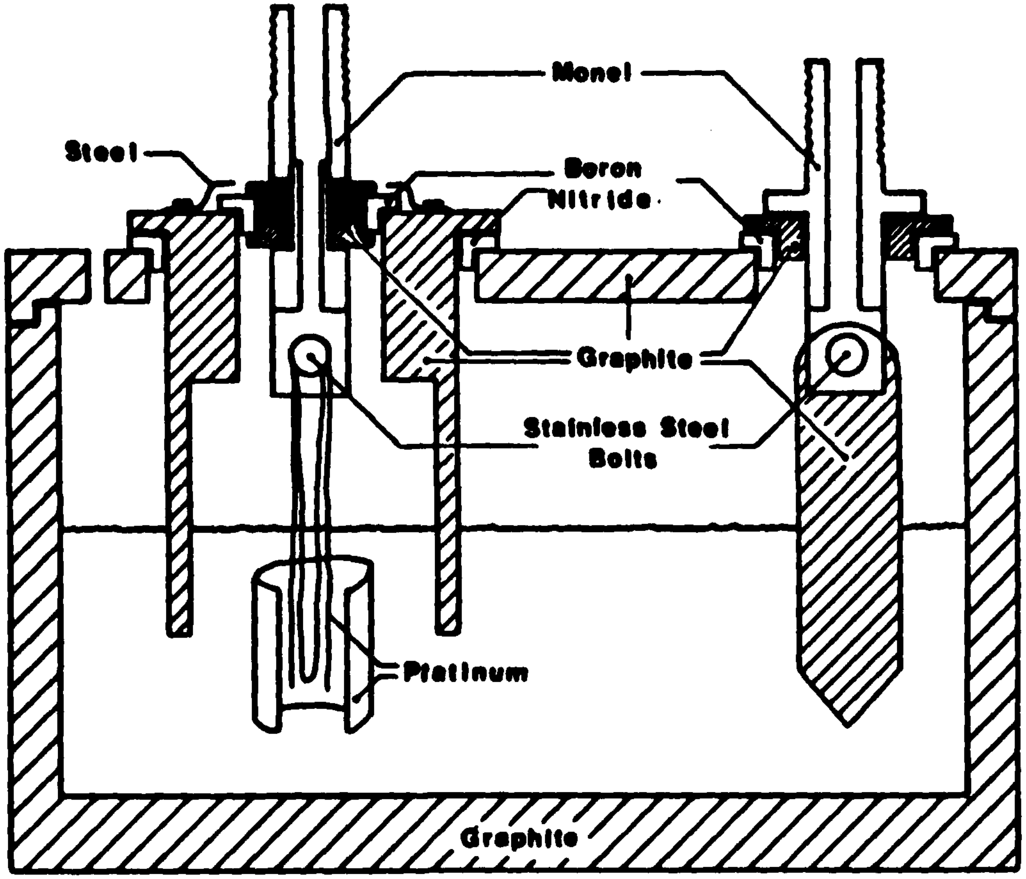


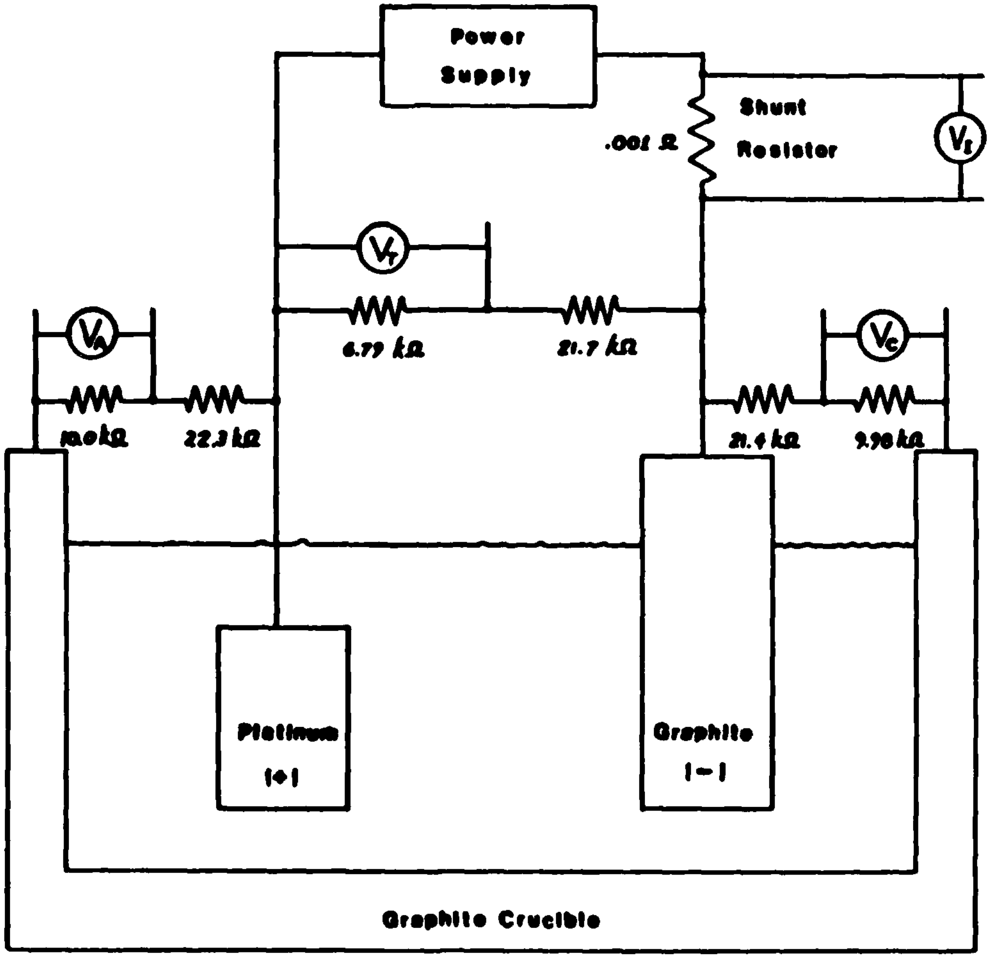
FLETCHER, FIGURE 12



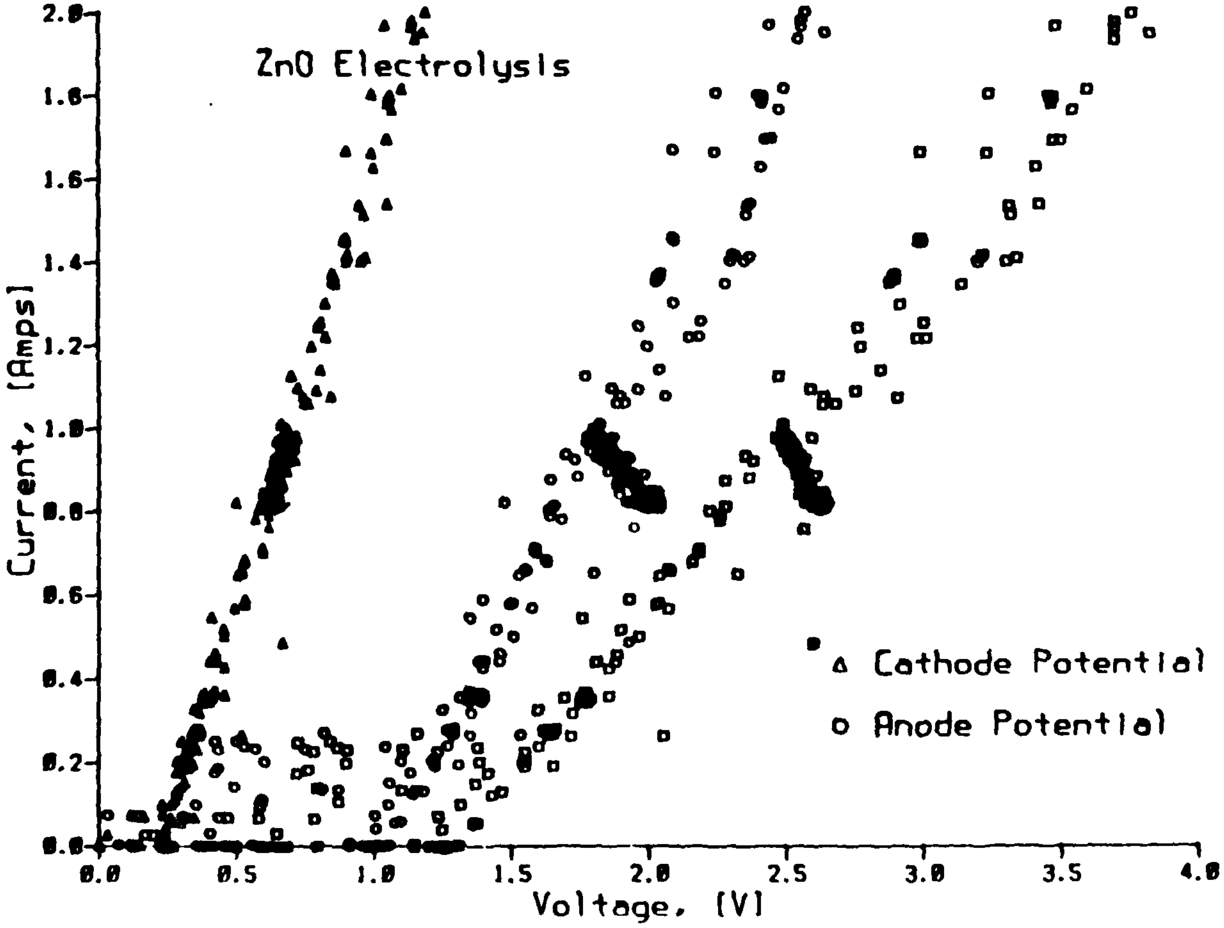
FLETCHER, FIGURE 13



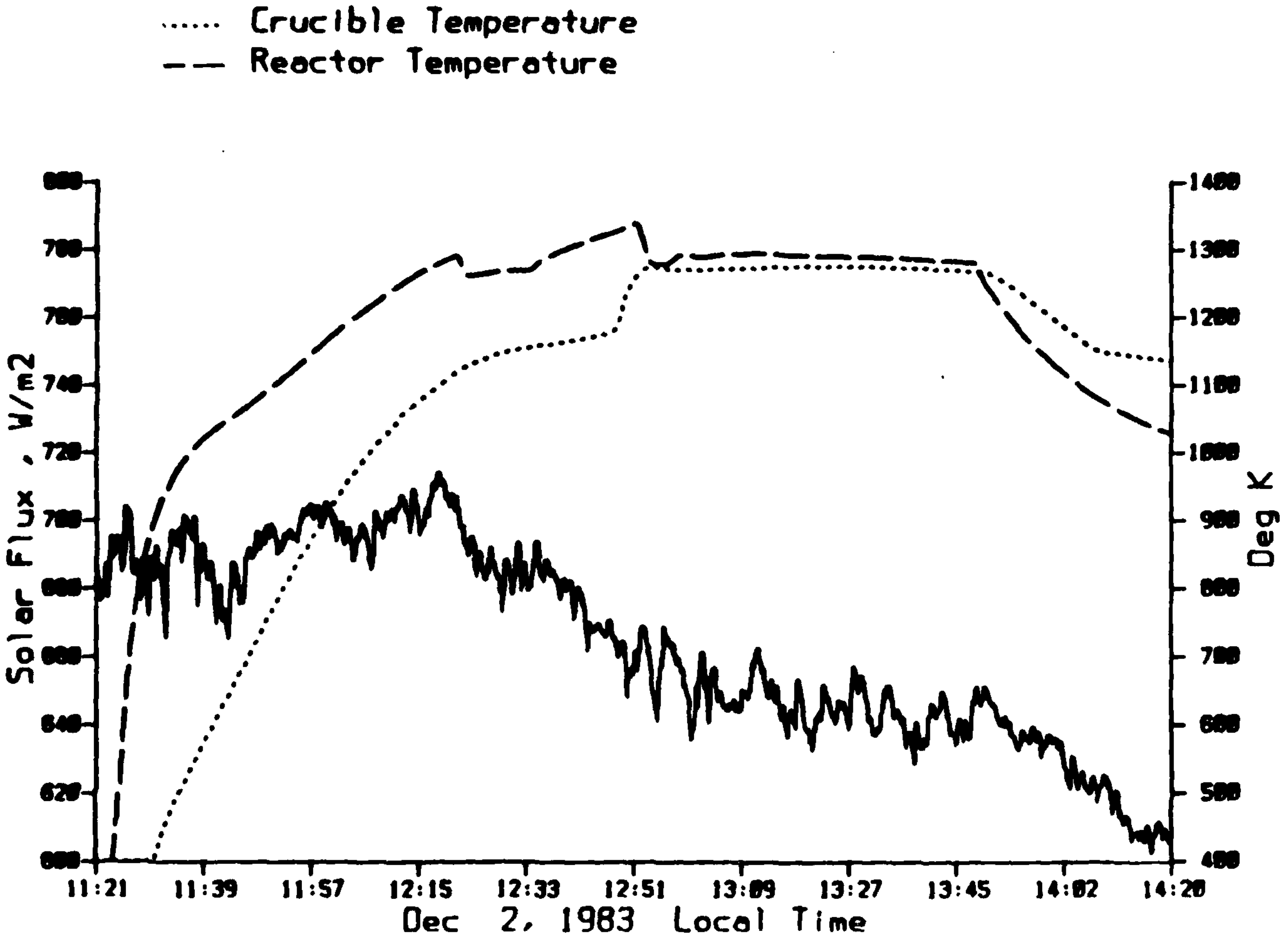
FLETCHER, FIGURE 6



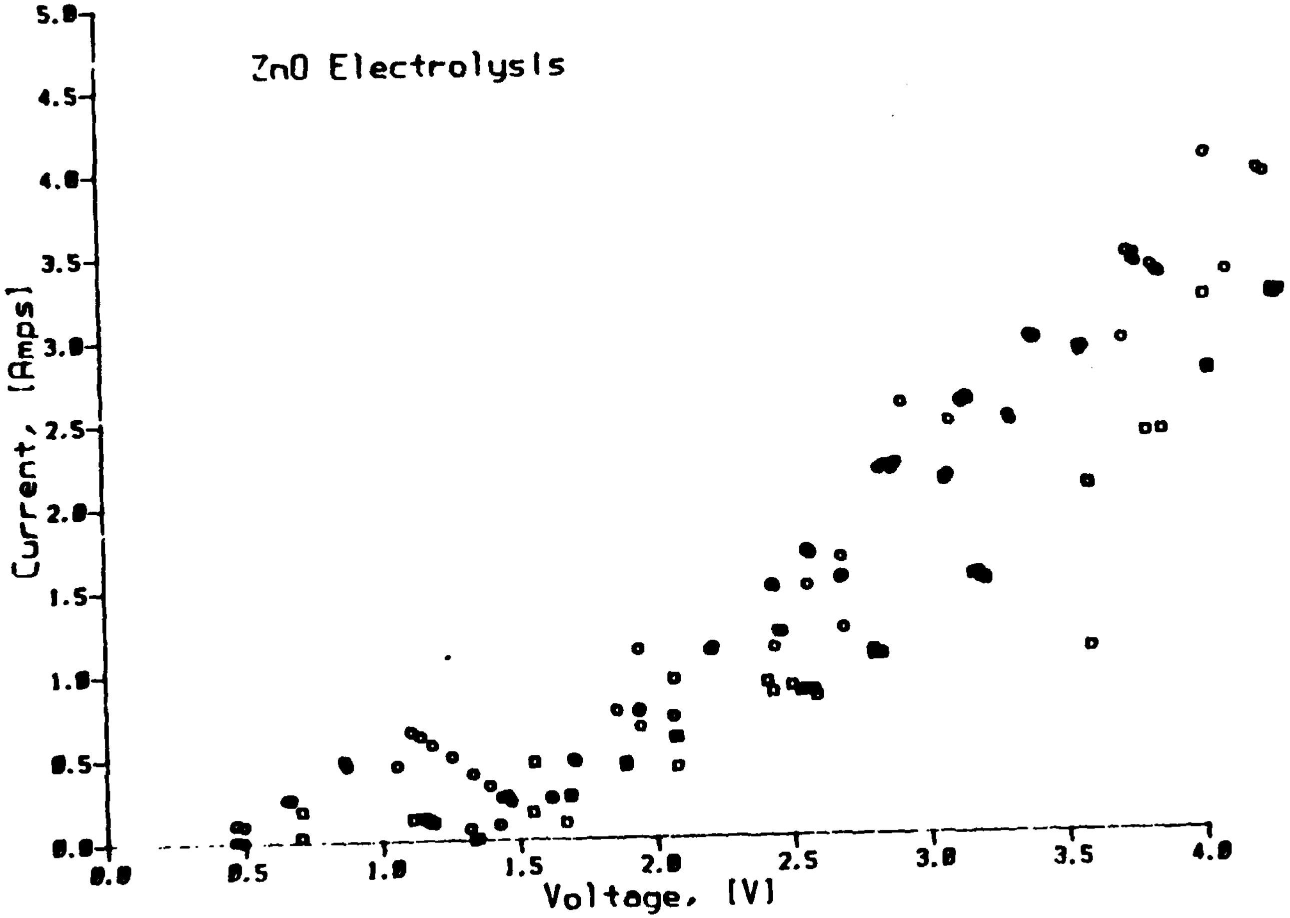
FLETCHER, FIGURE 7



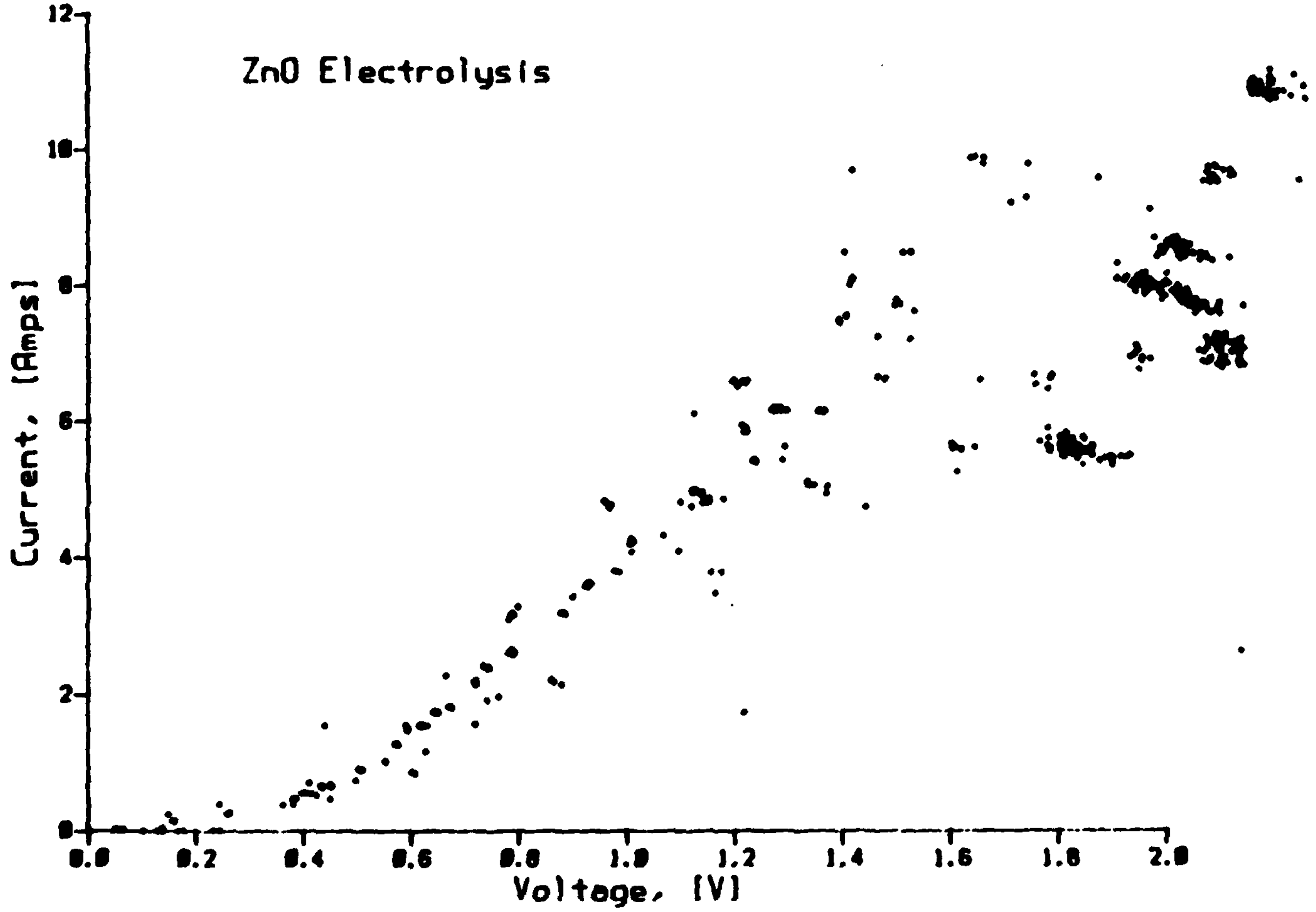
FLETCHER, FIGURE 14



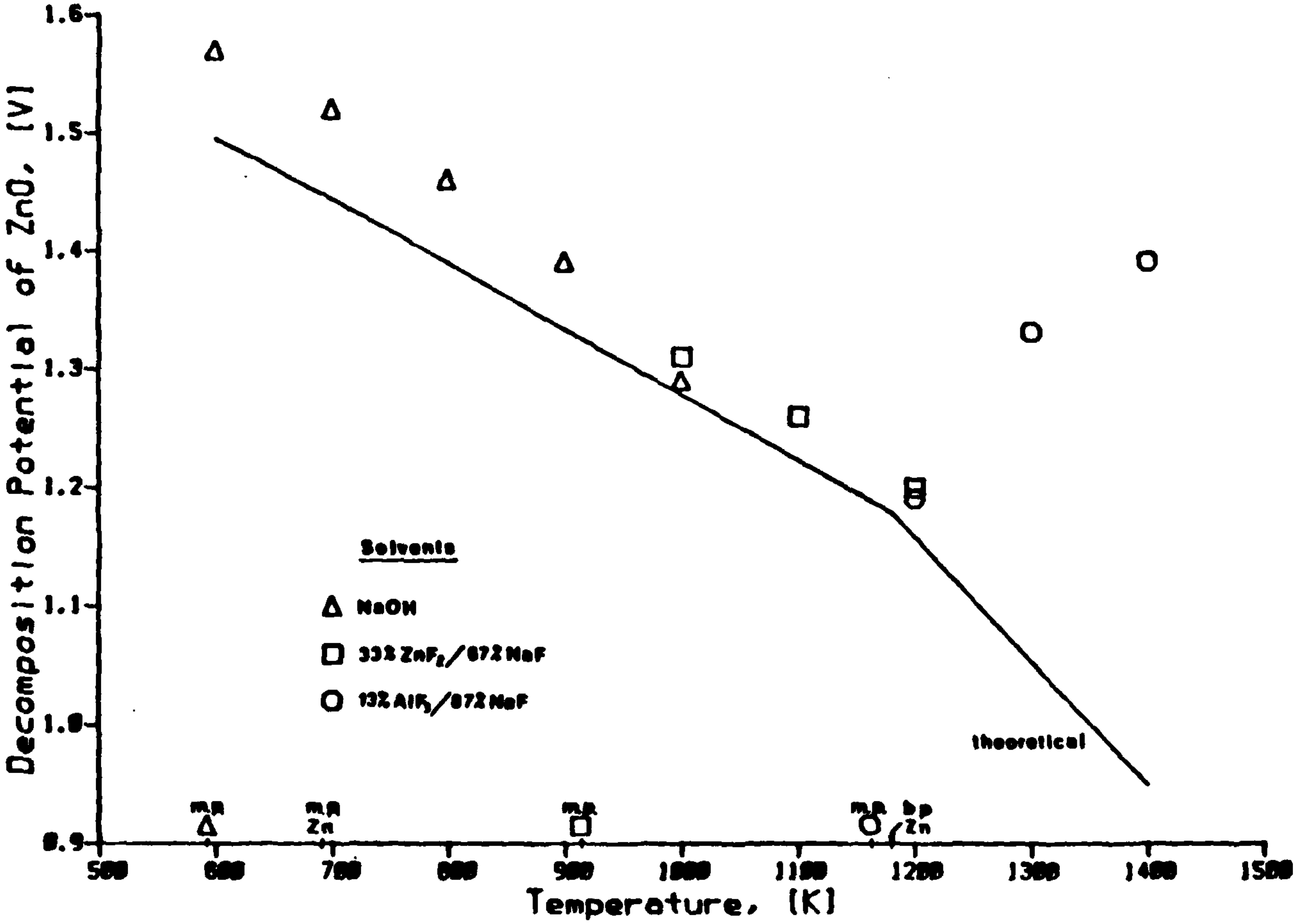
FLETCHER, FIGURE 8



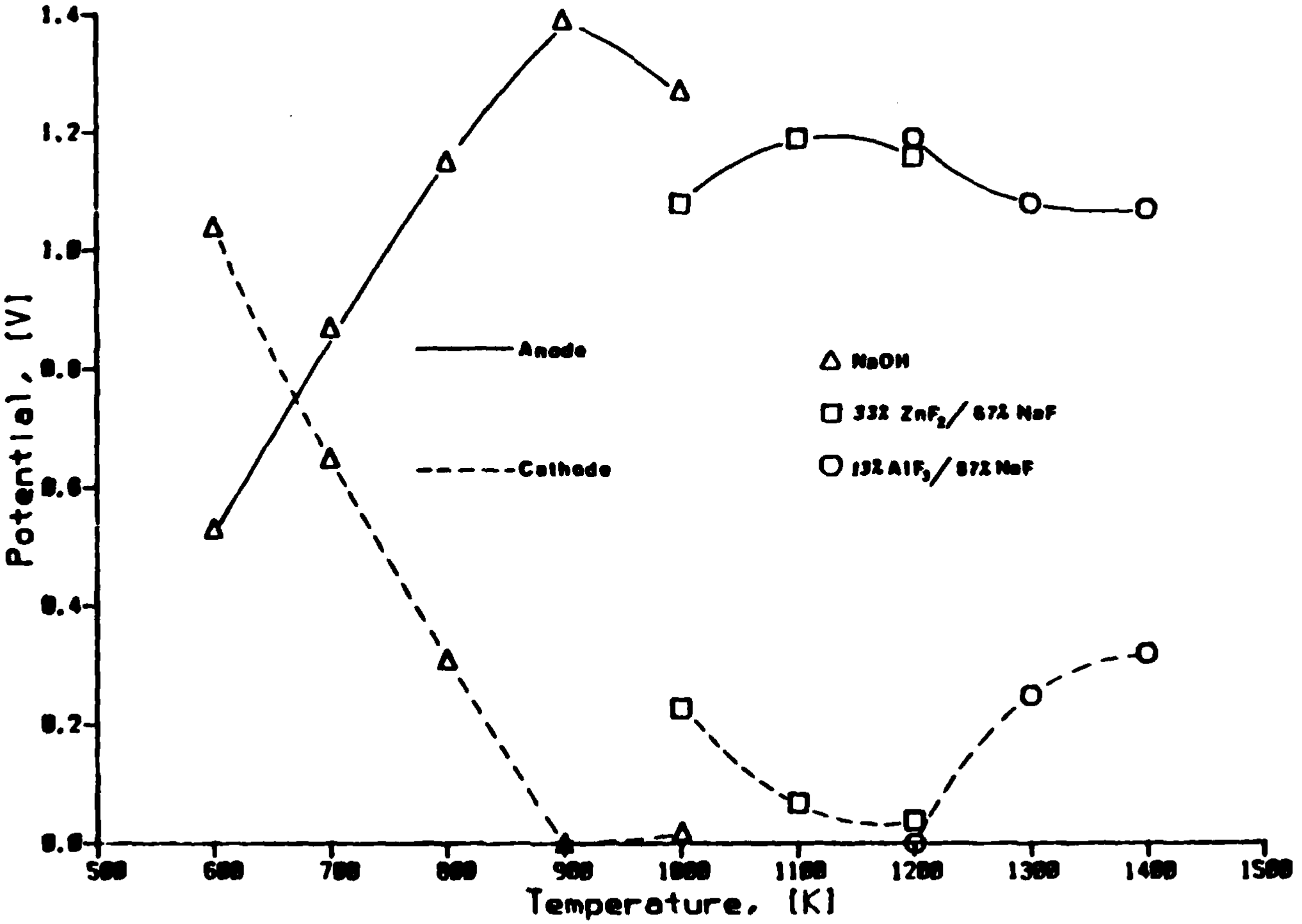
FLETCHER, FIGURE 15



FLETCHER, FIGURE 9



FLETCHER, FIGURE 16



FLETCHER, FIGURE 17