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*Research was sponsored by the Division of Waste Products, Office of Nuclear Waste Management, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

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ABSTRACT

An process for separating tritium from light and heavy water is described. Hydrogen is transferred at and through bipolar electrodes at rates H > D > T. In a cell containing several bipolar electrodes placed in series between two terminal electrodes, a flow of hydrogen is established from the terminal anode compartment toward the terminal cathode. An electrolyte feed containing tritium is continuously added to the system and is subsequently transported countercurrent to the hydrogen mass transfer. A cascaded system is established, in which effluent streams enriched and depleted in tritium can be withdrawn. The voltage drop is smaller at any bipolar electrode as compared to the voltage for normal electrolysis. Cell design is compact because isotope separation occurs at bipolar electrodes without evolution of gas. Isotope separation was demonstrated in laboratory cells where a steady-state tritium concentration gradient was attained. This gradient was in agreement with concentrations calculated from a derived mathematical model.

INTRODUCTION

The need to separate tritium from other hydrogen isotopes, either in the form of elemental hydrogen or in the form of water, arises in various aspects of nuclear technology:

1. Removal of tritium from waste light water in nuclear fuel reprocessing facilities,
2. Removal of tritium from heavy water serving as a moderator in pressurized heavy water reactors (PHWR),
3. Concentration of tritium from contaminated light and heavy water to a level suitable for further enrichment for various applications such as fuel for fusion reactors, and
4. Fusion reactor fuel purification and recycle.

Although some methods for H-D separation are well developed and may be, in principle, applied to H-T and D-T separations, it is not practical to do so because of the radioactive nature of tritium which requires control and confinement. Various existing exchange processes appear to be cost effective, but they would require voluminous containment structures, the construction and maintenance cost of which would be prohibitive. Conventional electrolytic isotope separation is effective because of the large separation factors achievable. However, appreciably more power is consumed as compared to exchange processes; electrolysis also requires handling of large volumes of gases.

Because of the various process limitations described above, a bipolar electrolytic process was developed which exploits the advantage of high separation factors and simultaneously reduces the problems of gas handling and the high power consumption associated with normal electrolysis.

The concept of hydrogen isotope separation by bipolar electrolysis was proposed and discussed by several authors (1-4), but only limited conceptual studies (1-3) and experimental work (4) was performed. In this process hydrogen isotope separation occurs at bipolar electrodes which are permeable to elemental hydrogen; hydrogen formed by the electrochemical reduction of water at the cathodic surface permeates the electrode material and is oxidized to water at the anodic surface. No gases are evolved at the bipolar electrode surfaces. Mass transport is faster for the lighter isotopes, thus enrichment of the heavier isotope occurs in the remaining aqueous phase. In a cell containing several bipolar electrodes and two terminal electrodes (Fig. 1) a flow of hydrogen (W) is established from the terminal anode compartment toward the terminal cathode. At the terminal cathode hydrogen gas is evolved. Since oxygen is formed at the terminal anode, a net loss of water occurs only in the anode compartment. A tritium-containing feed (F) is continuously added to the terminal cathode compartment, and it is subsequently passed from one cell compartment to another in a countercurrent direction to the hydrogen mass flow. This results in a cascaded system where the stream (P), enriched in the heavier isotope, is withdrawn from the anode compartment. A stream depleted in the heavier isotope leaves the system in the form of hydrogen gas (W).

In this paper a mathematical model quantitatively describing the hydrogen mass flow and separative efficiency of the process is given. An estimate has been made of the power requirements for this process and the demonstration of feasibility on a laboratory scale using a multibipolar cell is presented.

POWER CONSUMPTION CONSIDERATIONS

A major advantage of the bipolar process is its ability to consume less power than equivalent conventional electrolysis. This reduction in power consumption is possible because of different electrochemical reactions occuring at and within the bipolar electrodes as compared with those of normal electrolysis. In conventional water electrolysis, the net standard potential is -1.229 volts, whereas the net standard potential for bipolar electrolysis is zero; the only additional potential which is required in both electrolytic processes is the "overpotential" necessary to drive the reaction at an appreciable rate.

A bipolar electrode cannot exist without the usual terminal electrodes, and therefore the total voltage of a multistage bipolar system will always include the voltage associated with one normal electrolysis cell. The voltage required to perform electrolysis at a specified rate is represented as E_e for normal electrolysis and E_{BP} for bipolar electrolysis. The total voltage in a multistage separation cascade with J normal electrolysis cells can be expressed as

$$\Sigma E_e = J\ E_e. \tag{1}$$

In the case of bipolar electrolysis, each passage of hydrogen through a bipolar electrode represents an isotope separation stage; thus in a cascade with J stages, there are (J-1) bipolar electrodes. Therefore the total voltage of a bipolar electrolysis cascade can be expressed as

$$\Sigma E_{BP} = E_e + (J-1)\ E_{BP}. \tag{2}$$

The influence of the terminal electrode voltage on the total voltage of a bipolar cascade can be expressed by the relationship between average voltage per stage and the total number of stages in a bipolar cascade. The average voltage can be defined as

$$E_{av} = \Sigma E_{BP}/J = \frac{E_e + (J - 1)\, E_{BP}}{J} \tag{3}$$

As one increases the number of stages in a bipolar cascade, the average voltage per stage approaches the value of E_B as the number of stages increases to infinity. The smaller the value of E_{BP} compared to E_e, the less power will be consumed for the bipolar process compared to that for the normal electrolysis. However, most of the average voltage reduction is achieved with only a few separation stages.

Power consumption attributed to an electrolytic isotope separation cascade is not only a function of the total voltage that must be applied but is also dependent upon the total quantity of water that must be electrolyzed. In order to determine the power consumption required for isotope separation, consideration must be given to the specific separative task and to the design necessary to achieve the best approximation of an ideal separation cascade.

BIPOLAR ELECTROLYTIC SEPARATION CASCADE MODEL

A multibipolar electrolytic cell is inherently a "square" cascade: the electrode area per stage and the hydrogen mass flow through each bipolar electrode is identical. Using steady state cascade theory, a design equation can be derived specifically for bipolar electrolysis. The total enrichment of the heavy isotope for the enriching section of a square cascade with a flow scheme as shown in Fig. 1 may be expressed as

$$m_F = \beta m_p, \tag{4}$$

where

$$\beta = (1/\alpha\phi)^J + \frac{P}{F}\left[\frac{1 - (1/\alpha\phi)^J}{1 - (1/\alpha\phi)}\right], \tag{5}$$

m_F = mole fraction of heavy isotope in the feed,

m_p = mole fraction of heavy isotope in the product,

α = single stage bipolar separation factor,

P = molar flowrate of product; moles of hydrogen/unit time,

F = molar flowrate of feed; moles of hydrogen/unit time,

$$\phi = \frac{1}{1 - P/F}$$

J = total number of separation stages in a square section with stage number one being the bipolar electrode opposite the terminal anode and J being the terminal cathode.

Equation (5) may be used to calculate the number of stages (J) necessary to enrich the heavier isotope to a desired concentration. Also Eq. (5) may be used to calculate the interstage isotope composition in the electrolyte throughout the square cascade with a given product composition (m_p), single stage separation factor (α), and product-to-feed ratio (P/F).

Cascade theory predicts that an ideal separation cascade should be tapered from stage to stage with the maximum mass transport occurring at the feed point. This tapering is theoretically more efficient than a square cascade because total cascade volume and energy requirements are minimized. If a tapered cascade is not possible, its efficiency can be approximated by a "squared-off" cascade consisting of a series of square cascade sections of diminishing size connected in a series arrangement. The optimum number of separation stages required for a specific isotope enrichment can be determined by ideal cascade theory. The total number of square sections and the number of separation stages per square section can be arbitrarily selected, but the total number of separation stages in the squared-off cascade must equal the total number of stages of the ideal cascade. Using the mathematical model for a squared-off cascade (6), adjustment of the product-to-feed ratio for each square section can be made such that the product stream composition of a specific section matches that predicted by the ideal cascade. Once this procedure is implemented, the size of the separation cascade is fixed and the total power requirements for the assumed conditions can be calculated. The minimum power requirement for a particular enrichment is obtained by systematically repeating the above procedure and varying the number of square sections (6).

EXPERIMENTAL RESULTS

For efficient design of the bipolar separation cell, the choice of electrode material becomes critical. Among a variety of candidate materials, palladium-25% silver alloy was chosen as the most suitable material for experimental demonstration. When an appropriate surface treatment (7) was applied to the thin Pd-25% Ag electrode foils, sufficient activation of the surface was achieved to permit complete hydrogen dissolution and permeation at current densities of 0.3 amp cm^{-2} over a period of several weeks without significant hydrogen bubble formation. From known data on the solubility of deuterium and protium and their respective diffusion coefficients in Pd-25% Ag at various temperatures, maximum current densities could be calculated for varying electrode thicknesses. The maximum current density values observed at different experimental conditions coincided with those as calculated. Knowledge of maximum current density is necessary to estimate the electrode and cell dimensions required for a specific application of the process.

Although the standard potential for hydrogen transport through the bipolar electrode is zero, a potential drop across the electrode is necessary to operate the separative process at an appreciable rate. Using a single bipolar cell with Pd-H reference electrode probes near the bipolar electrode surfaces, the anodic and cathodic overvoltage were measured as functions of current density, temperature, electrolyte concentration, and electrode thickness. Measurements were made in both the H_2O and the D_2O systems; data are presented in Fig. 2 for a cell containing 6 N NaOH electrolyte in H_2O. Similar data were obtained for the NaOD-D_2O system, but the observed overvoltage was somewhat greater. When the maximum current density was exceeded, a sudden and significant increase in voltage at the anodic surface was noted (Fig. 2). This increased voltage occurred because the rate of hydrogen dissolution and permeation was insufficiently rapid to transport the hydrogen equivalent to that generated by the imposed current to the anodic surface. To compensate for the insufficient availability of hydrogen, oxygen was evolved from the anodic surface of the bipolar electrode, which reaction requires a higher anodic voltage than the oxidation of hydrogen sorbed in the electrode.

Experimental values of deuterium-tritium single bipolar separation factors (α_{DT}) at three different temperatures and at current densities of 0.21, 0.36, and 0.50 A cm^{-2} are given in Table 1. No significant dependence of α_{DT} on current density was found, and only small dependence on temperature was observed. Several measurements of the hydrogen-tritium separation factor, α_{HT} (see Table 1), were performed with little or no temperature dependence being noted.

Table 1. Hydrogen Isotope Separation Factors on a Single Bipolar Electrode

Temperature °C	α_{DT}	α_{HT}
30	-	11.7 ± 1.0
35	2.13 ± 0.05	-
55	2.09 ± 0.03	10.8 ± 0.7
90	2.02 ± 0.03	11.4 ± 0.5

Several multibipolar electrode cell designs were tested. The electrolyte feed was supplied by a metering pump. A sectional view of one of the multibipolar cell assemblies is shown in Fig. 3. The cell body consisted of several polysulfone blocks with channels machined in each block to provide a passage for electrolyte flow from one compartment to the next. The bipolar electrodes were sandwiched between the blocks forming the cell compartments and were gasketed with porous Teflon sheet. The terminal electrode compartments were made higher (greater volume) than the intermediate compartments to allow space in which the foam caused by the evolving gases could be dissipated. Teflon heat-exchanger tubing (not shown in Fig. 3) inserted through the cell walls provided control of the electrolyte temperature. Initially, the cell was filled with electrolyte of equal tritium concentration to that which would be fed continuously to the cell during the experiment. The bipolar electrodes were cathodically charged with hydrogen (using a current density of 0.05 A cm^{-2}) until gas bubbles appeared at the surfaces.

In a typical experiment a constant current flow of 0.3 A cm^{-2} was applied to the terminal electrodes and the cell was operated until a steady-state isotope composition was attained. Samples were taken on a daily basis from the anode compartment for tritium analysis by scintillation counting. After reaching a steady-state concentration profile, as indicated by the constancy of the tritium concentration in the anode compartment, the experiment was terminated and the isotopic composition of the electrolyte in all compartments was determined. Experimental data from one such experiment are shown in Fig. 4. The concentration of tritium in the waste stream (W) was 1.18 μc/mole H_2 during the entire experiment. The ratio of the tritum content of the product stream at steady state (77.76 μc/mole H_2) and that of the waste stream yielded a separation of 65.9 across the cascaded cell. Sodium hydroxide, which would otherwise accumulate in the anode compartment was continuously removed by conversion to sodium carbonate using CO_2 gas in a spray reactor evaporator. Water, as it was removed from the sodium carbonate by evaporation, was returned to the anode compartment with no added electrolyte.

DISCUSSION

Confirmation that a lower voltage drop across a single bipolar stage as compared to that of a single conventional electrolysis cell was observed experimentally. The single bipolar stage voltage (E_{BP})* was found to be 1.17 V as compared with 2.12 V (E_e) (8, 9) for an average voltage in a normal cell under comparable conditions. By effective surface activation, very high current densities have been achieved resulting in a very compact cell design with less expenditure for the electrode material than had been originally anticipated.

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*Bipolar stage voltage is the sum of the voltage across a 0.025-mm thick Pd-25% Ag electrode and the ohmic contribution of the electrolyte between two electrodes of 6-mm spacing at 84°C, 6 N NaOH, and 0.3 amp cm^{-2} current density.

To estimate power conservation for a given bipolar separative system, power consumption must be compared to that required to operate an equivalent number of conventional electrolysis cells. One such analysis was made for the particular case of tritium removal from heavy water used as a reactor moderator and coolant (9). In this case the objective was to reduce the steady state tritium content in the coolant from 20 Ci/l to approximately 3.3 Ci/l, and simultaneously to enrich the tritium to 10 mole percent; at this latter concentration other established, less costly methods could be used to subsequently obtain pure tritium. The total electrical power required for a squared-off cascade system for this example was calculated to be approximately 75% of that consumed in normal electrolysis (8). This estimate was based on the present "state of the art" for bipolar electrolytic separation. Much faster hydrogen diffusion and lower anodic voltage would be expected if satisfactory porous metal electrodes were developed.

Hydrogen isotope separation at the Pd-25% Ag bipolar electrode represents a modified case of normal electrolytic separation; in both cases the initial reaction is the electron transfer from the electrode to a water molecule. In the bipolar electrode process the hydrogen atom is subsequently sorbed into the electrode material; in normal electrolysis it combines with another hydrogen atom to form hydrogen gas at the electrode surface. These mechanisms which follow the initial electron transfer can influence the separation factor of the overall process. Our experimental results indicate that the magnitude of the bipolar separation factor is comparable to that observed in normal electrolysis. It was found however that the values of bipolar separation factors are much less dependent on temperature than those reported for normal electrolytic separation. This conclusion is of importance in that the operation of a bipolar system at high temperature and high current density is necessary to achieve high mass transport, and these conditions can be achieved without significant loss of separative efficiency.

Results of a few experiments performed using multibipolar cells are in agreement with those predicted by the mathematical model used to describe a square cascade with the exception that measured H-T separation factors for a single stage were found to be smaller than expected from single bipolar electrode experiments (6.3 and 6.8 compared to 11). By comparison, a multibipolar electrode experiment in which protium and deuterium were separated yielded the same separation factor $\alpha_{HD} = 5$ as a single bipolar cell. It is postulated that the observed decrease in the H-T separation factor was not an intrinsic characteristic of the multibipolar cell concept, but that it was caused by a small degree of intermixing of water vapor from adjacent cell compartments.

CONCLUSIONS

Palladium-25% silver alloy was found to be a suitable construction material for laboratory-scale bipolar electrodes. Single bipolar separation factors under the conditions required for large-scale operations were found to be of satisfactory magnitude and reasonably constant with fluctuating experimental conditions. The calculated material flow, as derived from the squared-off cascade model, together with the voltage drop through the bipolar electrodes show that about 20-30% less power would be required for the bipolar electrolysis process as compared to normal electrolysis. The above conclusions have been reached with regard to the present research status of this process. An even greater reduction in the voltage drop through the bipolar electrode may be possible with porous electrodes; research in this area needs to be performed. The simplicity and efficiency of a multibipolar cell has great potential for designing a very compact separation facility.

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FIGURE CAPTIONS

Fig. 1. Schematic representation of a multibipolar cell.

F = Tritium-containing feed stream flow rate.

W = Waste stream flow rate (tritium depleted), and/or the amount of hydrogen passing through each bipolar electrode.

P = Product stream flow rate (enriched in tritium).

F = W + P.

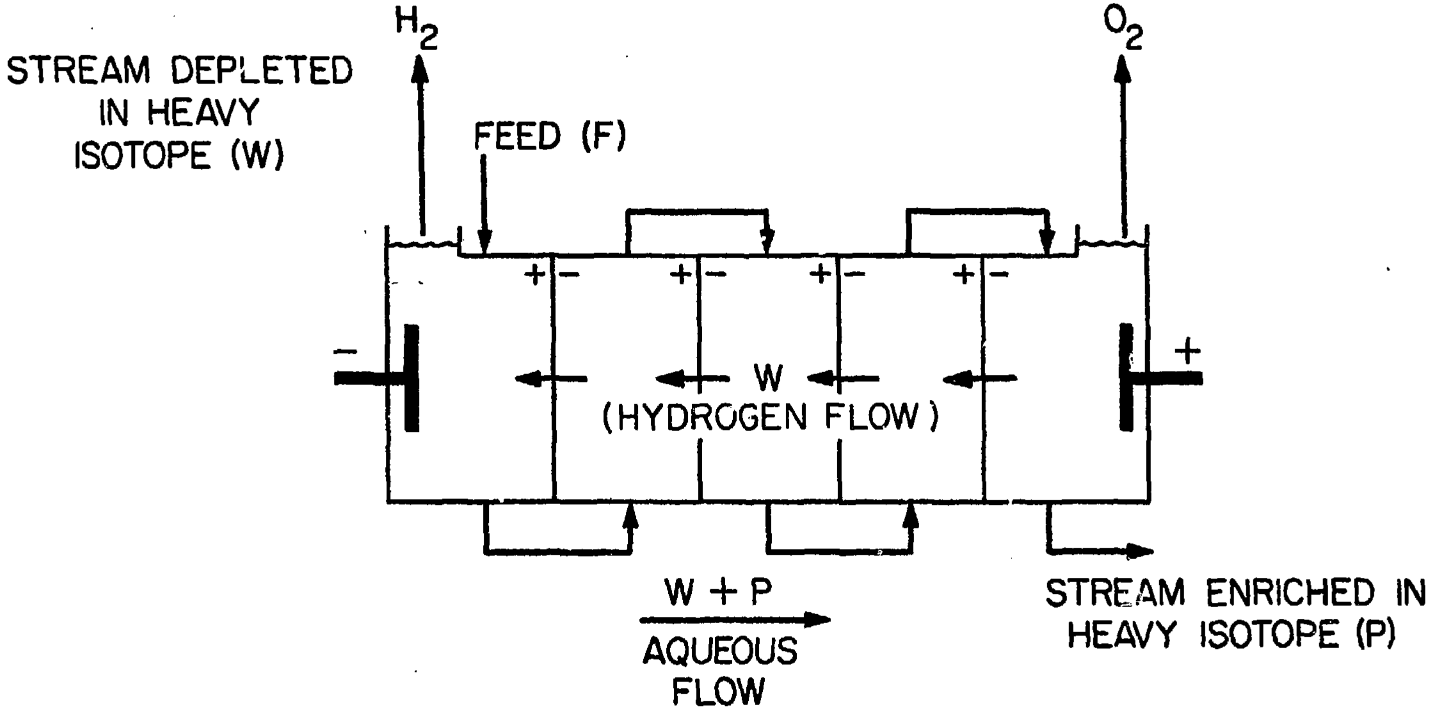
Fig. 2. Sum of the anodic and cathodic voltage drop at the bipolar electrode as a function of current density. Maximum current density is exceeded at the 7.6 x 10^{-3} cm thick electrode at 40°C and a current density >0.2 A cm^{-2}.

Fig. 3. A cross sectional drawing of a three-stage bipolar cell. The terminal anode (not shown) is positioned on the right end of the cell parallel to the terminal cathode. F, P, and W have equivalent meaning as in Fig. 1.

Fig. 4. Interstage tritium concentrations of a three-stage square cascade after reaching steady state condition.

ORNL-DWG 78-2833R2

SCHEMATIC FLOW DIAGRAM OF A BIPOLAR ELECTROLYSIS CASCADE FOR HYDROGEN ISOTOPE SEPARATION



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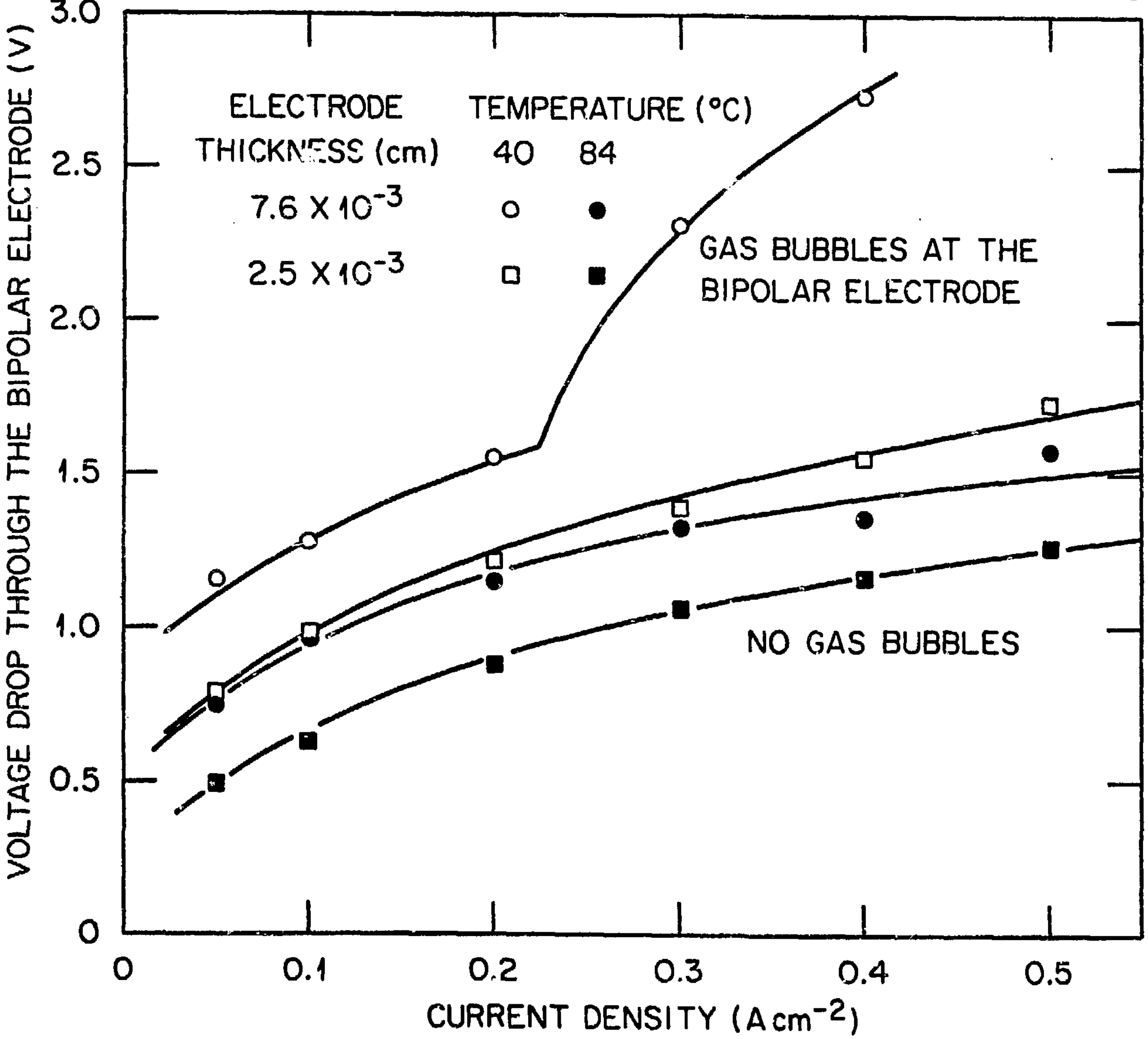

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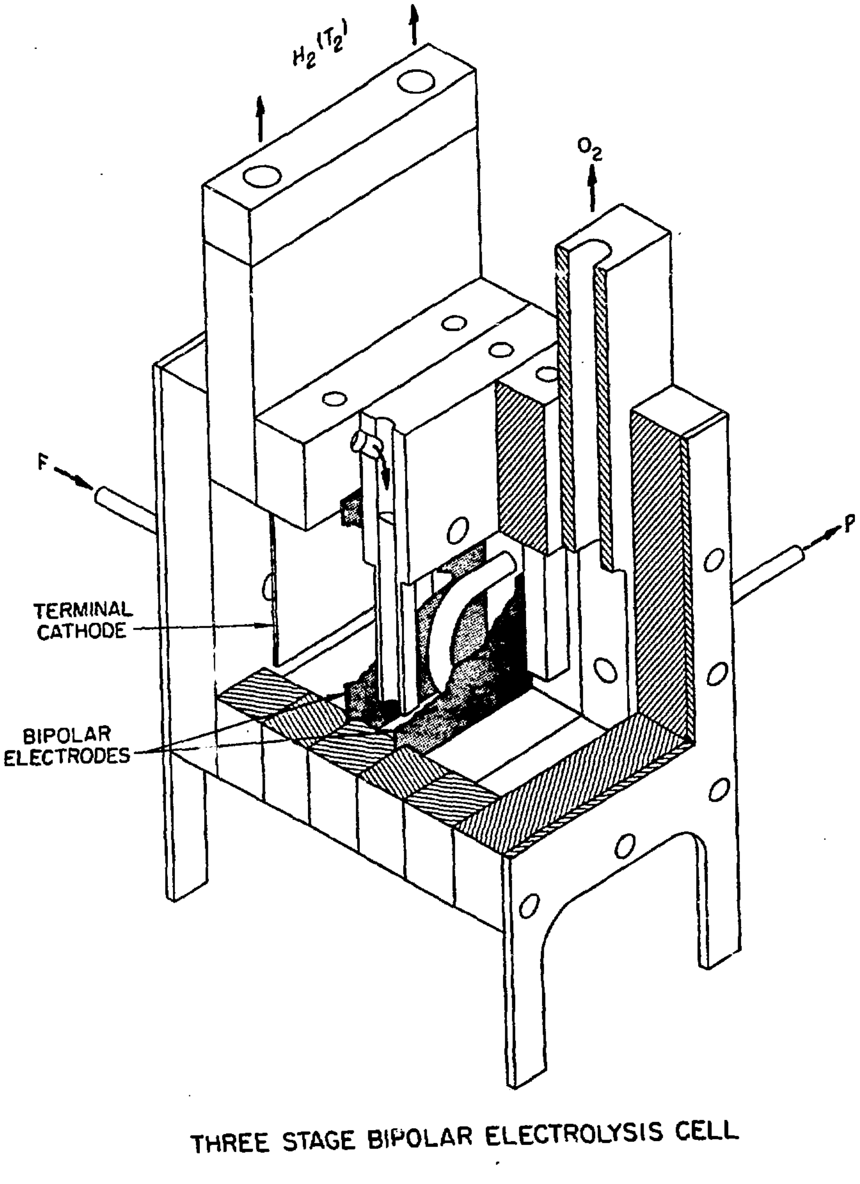

THREE STAGE BIPOLAR ELECTROLYSIS CELL

ORNL–DWG 79–14218R

MEASURED INTERSTAGE COMPOSITIONS IN THE MULTIBIPOLAR EXPERIMENTS SHOW EXCELLENT AGREEMENT WITH THE CALCULATED CONCENTRATION PROFILE