JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 477–488

Tritium separation from light and heavy water by bipolar electrolysis

M. PETEK, D. W. RAMEY, R. D. TAYLOR

Oak Ridge National Laboratory, Solid State Division, Oak Ridge, Tennessee 37830, USA

Received 15 September 1980

Using multiple bipolar electrolytic separation of hydrogen isotopes with Pd–25%Ag electrodes, the mathematical feasibility of this method for tritium separation was shown and experimentally verified. Separation factors were measured on single bipolar electrodes and were found to be approximately equivalent to those associated with individual ordinary electrolytic systems. Multibipolar separations were experimentally achieved in single cascaded cells in which each bipolar electrode was of equal area to others in a series arrangement. Factors measured for multibipolar H–D separation were close to the values measured in single-stage cell measurements; for H–T separation, interstage leakage reduced the measured separation factor. However, in both cases separation of sufficient magnitude was achieved to show feasibility for real application to the extraction of tritium from large-volume systems at high current density.

1. Introduction

The need for tritium separation from other hydrogen isotopes arises in a variety of nuclear technologies. For example, separation of tritium from light and heavy water moderated reactor coolants is desirable for biologic and environmental reasons. Enrichment of tritium for use in fusion systems and the subsequent repurification and recycling of such fuel will be mandatory.

Several processes for separating hydrogen isotopes have already been developed and are potentially available for this purpose [1], e.g., catalytic exchange between hydrogen gas and H_2O, H_2S, or NH_3, electrolysis, combined electrolysis and catalytic exchange, and distillation. The choice of a particular process depends on the specific application, e.g., which isotopes are to be separated (H–D, H–T or D–T), the amount of material to be processed, or the enrichment and/or depletion requirements. Although some methods for H–D separation are well developed and may be, in principle, applied to H–T and D–T separations, it may not be practical to do so because of the radioactive nature of tritium, which requires control and containment. Various isotope exchange processes appear to be cost effective, but they would require voluminous containment facilities, the construction and maintenance cost of which would be prohibitive. Conventional electrolytic isotope separation is effective because of the large separation factors that can be achieved. However, appreciably more power is consumed using electrolysis than when using the various exchange processes; electrolysis also requires the handling of large volumes of gases.

Because of several process limitations associated with conventional electrolysis and/or exchange, a bipolar electrolytic process has been suggested [2–8] which exploits the advantage of high separation factors and simultaneously reduces the problems of gas handling and high power consumption associated with normal electrolysis. This paper contains an explanation of the concept of bipolar electrolysis with countercurrent flow of hydrogen and water, statements of the basic requirements for its operation, experimental results which demonstrate the fulfillment of these requirements, and a discussion of its possible application in one specific case.

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2. Basic concept

2.1. *The bipolar electrode*

The essential feature of bipolar electrolytic separation of hydrogen isotopes is the use of a special bipolar electrode: it must be permeable to elemental hydrogen, but impermeable to water. Materials which meet these conditions are, for example, palladium and palladium-alloy foils and hydrophobic porous electrodes such as those used in fuel cell technology. Kinetic processes which take place at a bipolar electrode, as shown in Fig. 1 for a palladium electrode, are:

(a) Electrochemical reduction of hydrogen ion from water at the cathodic surface;

(b) Permeation of elemental hydrogen through the electrode material; and

(c) Electro-oxidation of hydrogen contained in the electrode at the anodic surface.

The net result is transfer of hydrogen ions from the aqueous phase on one side of the electrode to the other side. The overall rate of hydrogen transfer is faster for lighter hydrogen isotopes, thus isotope separation takes place.

2.2. *Separation factor*

Effectiveness of the separation process is defined by the magnitude of the separation factor α. The isotope separation factor is the ratio of the molar ratio of the light to heavy isotope in the phase leaving system (II) to the molar ratio of the light to heavy isotope remaining in system (I):

$$\alpha_{\mathrm{HD}} = \frac{([\mathrm{H}]/[\mathrm{D}])_{\mathrm{II}}}{([\mathrm{H}]/[\mathrm{D}])_{\mathrm{I}}} \tag{1}$$

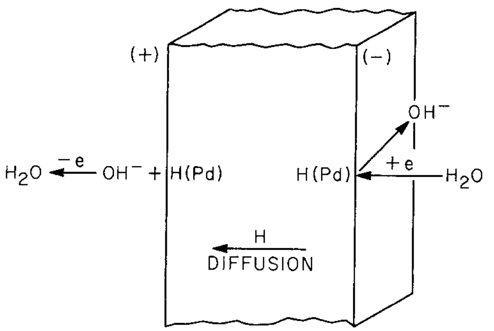

Fig. 1. Hydrogen transfer mechanisms at and in a palladium bipolar electrode.

$$\alpha_{\mathrm{HT}} = \frac{([\mathrm{H}]/[\mathrm{T}])_{\mathrm{II}}}{([\mathrm{H}]/[\mathrm{T}])_{\mathrm{I}}} \tag{2}$$

$$\alpha_{\mathrm{DT}} = \frac{([\mathrm{D}]/[\mathrm{T}])_{\mathrm{II}}}{([\mathrm{D}]/[\mathrm{T}])_{\mathrm{I}}}. \tag{3}$$

Equations 1–3 can be combined to yield

$$\alpha_{\mathrm{DT}} = \alpha_{\mathrm{HT}}/\alpha_{\mathrm{HD}}. \tag{4}$$

A theoretical relationship between α_{HD} and α_{HT} which may be applied to electrolysis was derived by Bigeleisen [9]:

$$\ln\alpha_{\mathrm{HT}}/\ln\alpha_{\mathrm{HD}} = 1.38 + 0.06/\ln\alpha_{\mathrm{HD}}. \tag{5}$$

This relationship has been confirmed for a wide range of experimental conditions [10, 11]. Thus, knowing the separation factor of one of the isotope pairs under specific experimental conditions, the separation factors of the other two isotope pairs may be estimated adequately using Equations 4 and 5.

The only hydrogen isotope separation factors for bipolar electrodes reported in the literature are those determined by Salmon [2] on palladium ($\alpha_{\mathrm{HD}} = 4.5$) in H_2SO_4 at 25° C and at 0.006 A cm^{-2} current density, by Dandapani and Fleischmann [12] on 0.1 mm thick palladium ($\alpha_{\mathrm{HD}} \sim 10$) with nonspecified constant current density imposed at the cathodic surface and constant potential (+ 0.025 V versus Pd–H_2 reference electrode) imposed on the anodic surface, and by Drazic [4] on carbon ($\alpha_{\mathrm{HT}} = 8$) in NaOH at 0.06 A cm^{-2} current density. Brodowsky *et al.* [13] have measured the individual H–D separation factors for the anodic, cathodic, and diffusion processes by placing an aqueous electrolyte solution on one side of the Pd–25%Ag membrane electrode and exposing the other side to hydrogen gas. In the diffusion experiment the Pd–25%Ag membrane was placed between two hydrogen gas compartments under a pressure differential. They found the H–D separation factor of the cathodic process followed by diffusion of hydrogen through the electrode to be temperature dependent, it being 7.8 and 13.1 for 60 and 0° C, respectively. In contrast, the separation factor for the diffusion process followed by oxidation was found to be considerably smaller at 1.7, independent of temperature, and practically identical in value to that for diffusion only (1.6) in the same temperature range. Because of the minimal published bipolar separation factors on Pd–25%Ag electrodes, this work will report the experimentally determined separation factors under conditions of high hydrogen throughput.

2.3. *Power consumption*

It can be expected that less power is consumed at a bipolar electrode than is consumed in conventional electrolysis. This power reduction is possible because of different electrochemical reactions occurring at and within the bipolar electrode as compared with those reactions occurring during normal electrolysis. During normal electrolysis, oxygen gas is formed at the anode, whereas in the bipolar process, hydrogen dissolved in the Pd–25%Ag alloy is oxidized to water. The corresponding cathodic reaction involves the reduction of hydrogen from water; for normal electrolysis the product is hydrogen gas and for bipolar electrolysis the product is elemental hydrogen dissolved in the metal electrode. Thus the standard potential for the overall reaction for normal electrolysis is 1.229 V whereas the net standard potential for bipolar electrolysis is zero. In order to drive the reaction at an appreciable rate, an overpotential must be superimposed on the standard potential for both electrolytic processes. Because of the difference in the standard potentials, the total voltage drop across a bipolar electrode can be expected to be considerably smaller than the voltage drop at the electrodes during normal electrolysis.

2.4. *Cascade separation*

Multiple isotope separations can be achieved in a single cell by placing several bipolar electrodes between two terminal electrodes, as illustrated in Fig. 2. The cell is filled with water containing a mixture of hydrogen isotopes and an electrolyte for conductivity. The voltage imposed between the terminal electrodes induces a flow of hydrogen through the system from the terminal anode compartment towards the terminal cathode with gaseous hydrogen evolving only at the terminal cathode.

Since a steady hydrogen flow is established throughout the system, water is removed by electrolysis only in the terminal anode compartment. Passage of hydrogen isotopes through a bipolar electrode occurs more rapidly for the lighter isotope (H > D > T), thus enrichment of the heavy isotope takes place in the remaining aqueous phase. Every bipolar electrode constitutes a separation stage, and since the evolution of hydrogen gas at the terminal cathode also favours the lighter isotope, the cathode represents an additional separation stage.

This multiple separation process can be made continuous by introducing feed at a steady rate F into the terminal cathode compartment (see Fig. 2), and continuously withdrawing two streams from opposite ends of the system. The stream of hydrogen that flows through the bipolar electrodes toward the terminal cathode is successively depleted in the heavy isotope, while a counter-

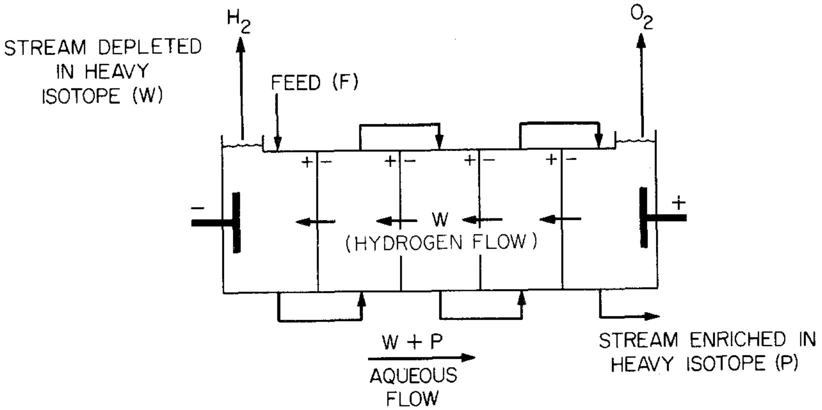

Fig. 2. A schematic flow diagram of a bipolar electrolysis cascade for hydrogen isotope separation.

current stream successively enriched in the heavy isotope is established by the flow of the aqueous phase toward the terminal anode. In this way a countercurrent multistage separation cascade is established in which streams enriched and depleted in the heavy isotope can be withdrawn from opposite ends of the system at rates P and W, respectively.

Such a multibipolar cell is inherently a 'square' cascade, i.e., the mass flow (as defined by the constant current flow) is the same throughout each separation stage. Because of uncertainties in the applicability of conventional cascade design equations to bipolar electrolysis, a mathematical model was derived specifically for multibipolar electrolysis [7]. Total enrichment (i.e., total increase in heavy isotope concentration from feed to product) for a square cascade may be expressed as

$$m_F = \beta m_P$$
$$\beta = (1/\alpha\phi)^J + \frac{P}{F}\left[\frac{1-(1/\alpha\phi)^J}{1-(1/\alpha\phi)}\right] \qquad (6)$$

where m_F = mole fraction of heavy isotope in the feed, m_P = mole fraction of heavy isotope in the product, $\phi = (1 - P/F)^{-1}$, α = single-stage bipolar separation factor, P = molar flow rate of product (total moles of hydrogen[†]/unit time), F = molar flow rate of feed (total moles of hydrogen[†]/time), and J = number of separation stages in a square cascade with the first stage being the bipolar electrode opposite the terminal anode. Equation 6 may be used to calculate the number of stages (J) necessary to enrich the heavy isotope to a desired concentration. When $P/F \ll 1$, β approaches the simplified expression $\beta = (1/\alpha)^J$.

3. Experimental

Palladium–25%Ag alloy was chosen in this work as the electrode material for the demonstration of the bipolar electrolytic hydrogen isotope separation process. Separation factors at single bipolar electrodes were determined under conditions permitting high hydrogen throughput, i.e., at high current densities and high temperatures. Special attention was given to the measurement of D–T separation factors because of the lack of experimental data in the literature for this isotope pair. Voltage drop across the bipolar electrode was measured as a function of current density, electrolyte composition, electrode thickness and temperature in order to establish parameters necessary for designing a separation cascade. Several multibipolar cells were designed and operated continuously.

3.1. *Instrumentation*

A PAR 371 potentiostat–galvanostat was used as a constant-current source during current–voltage measurements at a single bipolar electrode. Voltage drop between the bipolar electrode and the reference electrode was measured with a Keithley 173A multimeter. The constant-current source used in separation factor measurements was a modified H. P., Harrison 6205B dual power supply, and the current was integrated with a Curtis Instruments digital integrator, model 1002-SHR-C2. Temperature was monitored with a digital thermometer provided with a Teflon-encapsulated thermocouple inserted directly into the cell solution. For multibipolar cell experiments the constant current source was a Lambda power supply, model LK-350FM. Protium content in the D_2O system was determined by nuclear magnetic resonance (n.m.r.) using a Varian EM360A instrument. After neutralization of the alkaline samples with HCl, tritium content was determined by scintillation counting using a Packard Instagel cocktail in a Tricarb scintillation counter.

3.2. *Electrode material*

A palladium alloy containing 25 wt% silver was chosen as the electrode material because of its high permeability toward elemental hydrogen and its mechanical and chemical stability [14]. The 0.076 mm thick Pd–25%Ag foil electrodes were manufactured by Mathey Bishop Corporation in the form of a 100 mm wide strip. When thinner electrodes were needed, this foil material was rolled to the desired thickness.

[†] Total moles of hydrogen: the total molar flow rate of any two hydrogen isotope pairs: $H_2 + T_2$, $H_2 + D_2$ or $D_2 + T_2$.

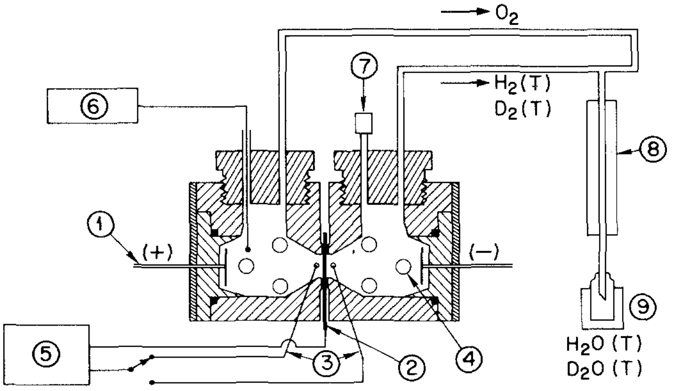

Fig. 3. Schematic representation of an electrolysis cell containing a single bipolar electrode. 1, Terminal electrode; 2, bipolar electrode; 3, reference electrodes; 4, heat exchanger; 5, voltmeter; 6, thermometer; 7, sampling port; 8, catalytic furnace; 9, cold trap.

3.3. *Single bipolar cell design*

Cells containing a single bipolar electrode between two terminal electrodes of platinum or palladium were constructed using Polysulfone† to resist corrosive attack by the caustic electrolyte. An illustration of the cell design is shown in Fig. 3. Prior to use, each electrode was annealed at 700° C in a hydrogen atmosphere for one hour, followed by surface activation using molten NaOH, as suggested by Serfass [15], in order to assure high surface permeation by hydrogen species. Minor variations in cell design were made depending on whether the cell was to be used for current–voltage measurements or for determination of separation factors. The cell body consisted of two identically machined Polysulfone blocks, sandwiched between two heavy aluminium plates. The whole assembly was held together by four bolts. The single bipolar electrode was placed between the blocks and gasketed with porous Teflon sheet (POREX, PTFE, P800, Glasrock Products, Inc.).

Platinum or palladium terminal electrodes were placed at each end of the cell in such a position that the gases evolved could freely leave the solution without contacting the bipolar electrode. Two palladium–hydrogen reference electrodes [16] were used to measure the voltage drop on each side of the bipolar electrode.

Electrolyte temperature in the cell was regulated by pumping thermostatted water through Teflon heat-exchange tubing inserted through the cell walls. When separation factor measurements were made, hydrogen and oxygen evolving at the terminal electrodes were mixed and chemically recombined at 300° C in a furnace containing a Pt-sputtered nickel–felt catalyst. Subsequently, water from this catalytic recombination was returned to the cathode compartment of the cell.

3.4. *Voltage drop and maximum current density (m.c.d.)† at the bipolar electrode*

The voltage drop at the bipolar electrode surface was measured using electrolyte concentrations of 3 N and 6 N NaOH in H_2O and 3 N NaOD in D_2O. Prior to using the palladium–silver foils as bipolar electrodes, each was saturated with hydrogen by connecting it temporarily as the cathode at a 0.05 A cm^{-2} current density until hydrogen bubbles appeared at its surface. Current densities between 0.05 A cm^{-2} and 0.50 A cm^{-2} were employed with bipolar electrodes of 0.025 mm and 0.076 mm thickness and 1 cm^2 electrode area. Electrolyte temperatures ranged from 40° C to 90° C. Under these conditions, the total cell voltage was measured after 30 minutes of operation at a specific current density. Current density was subsequently increased through the range noted above, and the first appearance of gas bubbles at the bipolar electrode was noted. The cumulative (anodic + cathodic) voltage drop as a function of current density, using two different electrode thicknesses and at two different temperatures, is shown in Fig. 4. A sharp increase was noted in the anodic voltage and consequently in the cumulative voltage across the bipolar electrode whenever gas bubbles appeared at the bipolar elec-

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† Polysulfone 'Udel' Union Carbide Corporation.

† Maximum current density (m.c.d.) is defined as that current density slightly below the value at which gas bubbles appear at the bipolar electrode surfaces.

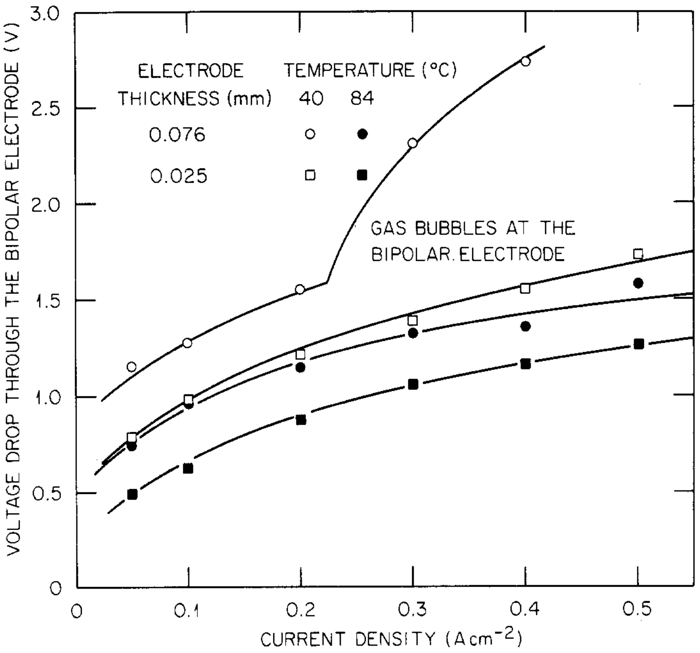

Fig. 4. Voltage drop across a Pd–25%Ag bipolar electrode as a function of current density. Electrolyte: 3 N NaOH in H_2O. (Data are expressed as the sum of the anodic and cathodic surface potentials.)

trode surface, i.e., when the m.c.d. was exceeded. No significant difference in the behaviour at the bipolar electrode was found when using 3 N or 6 N NaOH.

The effect of temperature on voltage across the bipolar electrode was measured at a constant current of 0.4 A cm^{-2} in the light and heavy water systems. High voltage across the bipolar electrode at low temperatures was accompanied by gas bubble formation which eventually ceased as the temperature was increased (Fig. 5); note that the voltage drop observed for the D_2O system is greater (~ 40% greater) than that for the H_2O system.

3.5. *Tritium separation factor at the bipolar electrode*

A known amount of tritium-containing 3 N NaOH or 3 N NaOD in H_2O or D_2O, respectively, was placed into the cell compartments. A constant

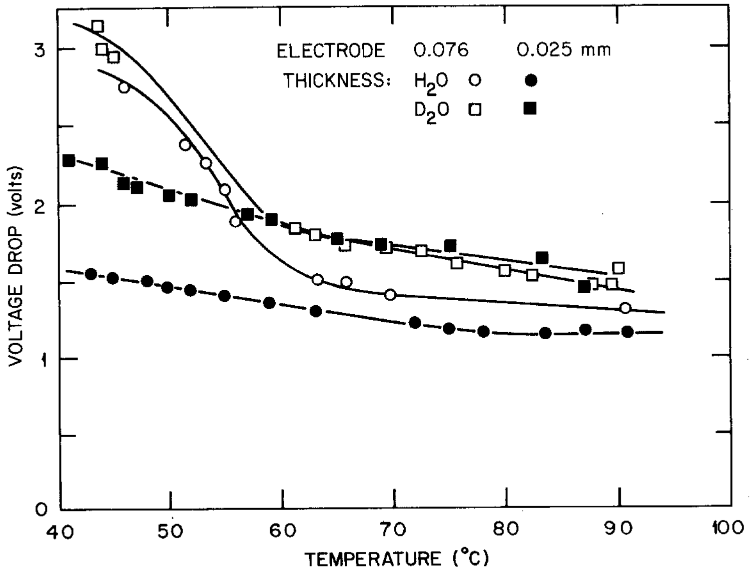

Fig. 5. Temperature dependence of the voltage drop across the bipolar electrode in the H_2O and D_2O systems. Current density: 0.4 A cm^{-2}, electrode thicknesses: 0.025 mm and 0.076 mm.

Table 1. Tritium 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

current was imposed across the single bipolar cell. Oxygen and hydrogen evolving at the terminal electrodes were recombined to water, and collected in a cold trap. These conditions were maintained until approximately one half of the solution within the anode compartment was electrolysed. In order to eliminate the contribution of isotope separation at the terminal cathode, the recombined water was weighed and returned to the cathode compartment at the end of each experiment. The separation factor was calculable from the isotope mass balance in both the anode and cathode compartments before and after the experiment [7]. The results are shown in Table 1. No significant effect of current density on separation factor values was observed.

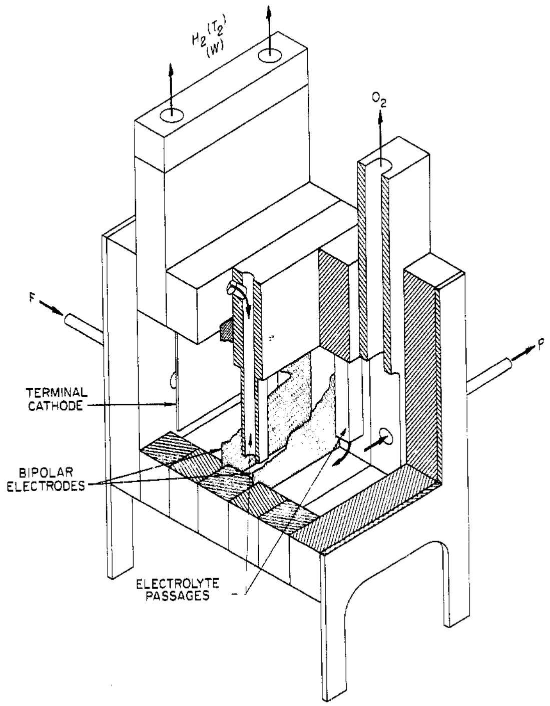

Fig. 6. Schematic representation of a multibipolar electrode separation cell.

3.6. *Multibipolar cell experiments*

A sectional view of a multibipolar cell assembly is shown in Fig. 6. 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 and therefore more voluminous than the intermediate electrolyte compartments to allow additional space in which to dissipate the foam caused by the evolving gases. Temperature was controlled by the method described for the single bipolar cell.

Several experiments were performed in laboratory-scale multibipolar cells operating continuously with a steady supply of NaOH-containing feed and a continuous product removal. In a typical multibipolar cell experiment, the cell was initially filled with water containing an electrolyte (NaOH) and a tritium concentration equal to that which would be added continuously to the cell throughout the experiment. After filling the cell, the bipolar electrodes were charged cathodically with hydrogen until saturation was achieved. The multibipolar cell was then operated at constant current until steady-state conditions were obtained, i.e., until a constant tritium activity in the product stream was achieved.

One experiment was performed with the following cell parameters: five separation stages (four bipolar electrodes plus the terminal cathode), electrodes with an area of 6.0 cm^2 each, 0.3 A cm^{-2} current density, and a cell temperature of 85 ± 5° C. This multistage system was fed with 19.43 cm^3/day of 3.3 N NaOH to the cathode compartment (1.105 mol H_2/day). The P/F ratio was 0.236 and the tritium content in the feed was 4.747 μCi mol^{-1} H_2. This separation system was operated for a total of 24 days, 8 of which were at steady state.

The single-stage separation factor for the above experiment was found by a trial-and-error solution of Equation 6 using the experimentally measured enrichment, β. The separation factor per stage for protium–tritium was calculated to be $\alpha_{HT} = 6.45$. At the end of this experiment, samples were taken from each interstage compartment and analysed

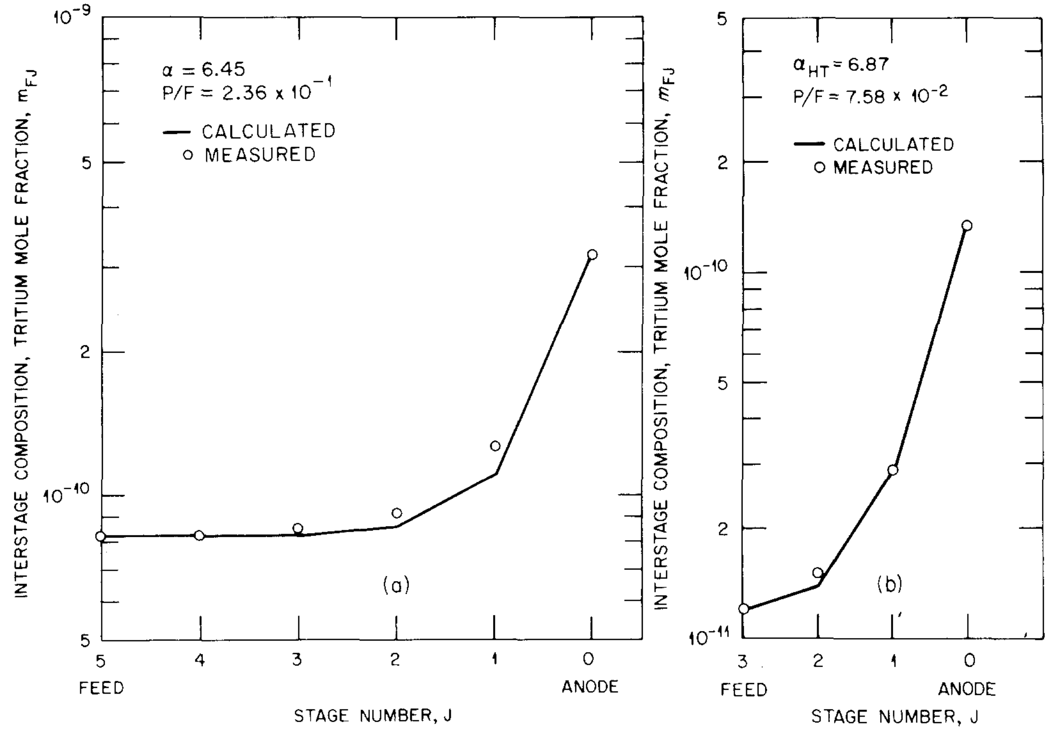

Fig. 7. Interstage tritium concentration of two three-stage cells after attaining equilibrium. Full lines represent calculated concentrations and the circles experimental values.

for tritium. Fig. 7a gives the measured concentration profile through the cascade. The experimentally observed tritium concentration between individual stages (circles) closely followed that predicted by Equation 6 (line); nearly all enrichment was observed to have taken place in the first two stages. The additional three stages would have been better utilized if a smaller *P*/*F* ratio had been used, but without a means of continuously removing electrolyte from the anode compartment, the *P*/*F* ratio was necessarily large in order to avoid solidification of the sodium hydroxide. The concentration of sodium hydroxide in the anode compartment (N_P) is governed by its concentration in the feed (N_F) and by the *P*/*F* ratio [i.e., $N_P = N_F/(P/F)$].

In another experiment with a larger electrode area (26.4 cm^2 each) and three separation stages (2 bipolar electrodes), a continuous electrolyte removal system was attached to the anode compartment so that a smaller *P*/*F* ratio could be used. Addition of the electrolyte removal system resulted in a slightly longer time needed to reach steady-state conditions as compared to the earlier experiment because of the additional effective volume of the anode compartment (30% increase). However, this same electrolyte removal system could accommodate a multistage system approximately 25 times larger than the one to which it was attached. Therefore, the addition of an electrolyte removal system of this type to a full-scale tritium separation facility would probably have a minimal effect on the time required to reach steady state.

Using 6.7 N NaOH containing 6.98 μCi tritium mol^{-1} H_2, the three-stage system was operated at a current density of 0.3 A cm^{-2} at 88.5 ± 2° C; a constant feed rate of 62.6 cm^3/day (3.54 mol H_2/day) was maintained. To hasten the rate of increase in tritium concentration in the system, no product was withdrawn during the initial part of the experiment except for the 0.5 cm^3/day necessary for analytical purposes. After 49 days of operation, the anode compartment reached a tritium activity of 77.76 μCi mol^{-1} H_2 (an enrichment of 11.14 times the feed concentration). At this point, the system was forced in to a steady-state condition by withdrawing more product (5.2 cm^3/day) and at the same time increasing the feed rate by the amount being withdrawn (feed rate increased to 67.8 cm^3/day). The system was operated for 8 days under these conditions to assure steady-state composition throughout the cascade. During the entire experiment the tritium concentration in the waste stream was 1.18 μCi mol^{-1} H_2 which amounted to a total enrichment between the product and waste streams of 65.9. The single-stage separation factor was found to be $\alpha_{HT} = 6.87$. Tritium concentrations in the interstage compartments at the end of the experiment are shown in Fig. 7b (circles); these data closely agree with tritium concentrations calculated using Equation 6 (line). An increase in tritium enrichment resulted with the lower P/F ratio (7.58×10^{-2}) (Fig. 7b) as compared to the previous multistage experiment (Fig. 7a), as was predicted by the theory.

4. Discussion

Palladium–25%Ag alloy foil was found to be a suitable electrode material for experimental demonstration of the bipolar hydrogen isotope separation process. When the molten NaOH etch treatment was applied to thin Pd–25%Ag foils, sufficient surface activation was achieved to permit complete hydrogen dissolution and permeation at current densities of 0.3 A cm^{-2} over a period of several weeks without significant hydrogen bubble formation. From known data on solubility of deuterium and protium and their respective diffusion coefficients in Pd–25%Ag at various temperatures [17–21], maximum current densities could be calculated for varying electrode thicknesses. The maximum current density values observed under different experimental conditions coincided with calculated values [7]. Knowledge of maximum current density would be necessary to estimate the electrode and cell dimensions required for specific applications of this process.

Palladium alloy electrodes, as is the case with metal electrodes in general, are subject to surface contamination over prolonged periods of operation. This contamination can attenuate the hydrogen sorption process with subsequent incomplete hydrogen transfer through the electrode. Therefore, long-term experiments are needed to establish the potential contaminants causing such process deterioration and to study the results of periodic *in situ* surface activation, such as the use of current reversal techniques. Surface contamination effects may be expected to be much less for porous electrodes of the fuel cell type. In addition, diffusion of hydrogen within such porous electrodes would be much faster than within the Pd-based foil electrodes with corresponding increased availability of hydrogen at the anode surface and lower overvoltage. Studies of porous bipolar electrodes would be necessary before complete analyses of the application and efficiency of this process can be determined.

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 [22–25]. Our experimental results indicate that the magnitude of the bipolar separation factor is comparable to that observed in normal electrolysis. However, it was found that the values of the 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 tranport, and these conditions can be used without significant loss of separative efficiency.

The H–T separation factors, as determined from two multibipolar cascade cell experiments and Equation 6, were found to be smaller than would have been expected from single bipolar electrode experiments (6.45 and 6.87 as 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 was found in 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 resulted from a small degree of intermixing of water between adjacent cell compartments during the experiments.

The actual isotope separation by bipolar electrolysis (a square cascade) was demonstrated in multibipolar cell experiments for the case of tritium in light water. The steady-state tritium concentration profiles for these experiments were calculated from the total enrichment using Equation 6 and were in excellent agreement with observed experimental data (Fig. 7). It was demonstrated that the separation efficiency can be increased by decreasing the P/F ratio, as would follow from Equation 6. It can be shown that the number of stages which can be efficiently utilized can be increased by a further reduction of the P/F ratio. In the case of tritium separation from heavy water, a considerably smaller single-stage separation factor ($\alpha \simeq 2$) would result. In this case, more separative stages could be efficiently utilized as compared to the number applicable to separation from light water for the same P/F ratio.

To estimate the power requirement for a given bipolar separative system, for comparison with that needed for normal electrolysis, the knowledge of the power consumption per separative stage and the total mass of hydrogen needed to be electrolysed is required. Let us assume that the voltage required to perform electrolysis at a specified rate is represented by E_e for normal electrolysis and E_{BP} for bipolar electrolysis. Both E_e and E_{BP} represent the voltage drop between two adjacent electrodes at a specific current density. The total voltage in a multistage separation cascade, with J normal electrolysis cells, can be expressed as

$$\sum E_e = JE_e. \tag{7}$$

In the case of bipolar electrolysis, the passage of hydrogen through each 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

$$\sum E_{BP} = E_e + (J-1)E_{BP}. \tag{8}$$

The average voltage per stage of a bipolar cascade approaches a minimum value of E_{BP} for an infinite number of stages. However, most of the advantage of decreasing the voltage per stage offered by bipolar electrolysis is achieved in the first four to eight separation stages. Values for E_e, given in Table 2, represent average cell voltages in modern commercial alkaline water electrolysers (5 N KOH at 80° C with 6 mm electrode spacing) as reported in the recent review by Lu and Srinivasan [26]. The E_e values for current densities greater than 0.3 A cm^{-2} were obtained by graphic extrapolation of the average current–voltage curve. Values for E_{BP} in Table 2 are the sum of the voltage drop across the bipolar electrode actually measured in this work (see Fig. 4) and the calculated voltage drop between two adjacent electrodes in a 6 N NaOH solution at 90° C and 6 mm inter-electrode distance. The conductivity data for concentrated NaOH at 20 to 200° C were taken from the work of Maksimova and Yushkevich [27]. Although the values of E_e and E_{BP} were measured and/or calculated under slightly different conditions, a direct comparison is instructive.

Table 2. Estimated separation stage voltage in normal and bipolar electrolysis at different current densities

Current density (A cm^{-2})	E_{BP} (V)	E_e (V)
0.05	0.53	1.70
0.1	0.65	1.81
0.2	0.90	1.98
0.3	1.17	2.12
0.4	1.36	2.22
0.5	1.54	2.29

0.025 mm thick Pd–25%Ag foil at 84° C.

It is apparent from Table 2 that lower voltage is required for bipolar electrolysis than normal electrolysis. However, the power consumption attributed to an electrolytic separation cascade is not only a function of the total voltage that must be applied but also of the total quantity of water that must be electrolysed. In order to compare bipolar electrolysis power consumption, consideration must be given to a specific separation task and how bipolar electrolysis can best approximate an ideal separation cascade.

Cascade theory dictates that an ideal separation cascade should be tapered [28] from stage to stage with the maximum cross section occurring at the feed point. This size 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 from the feed point,

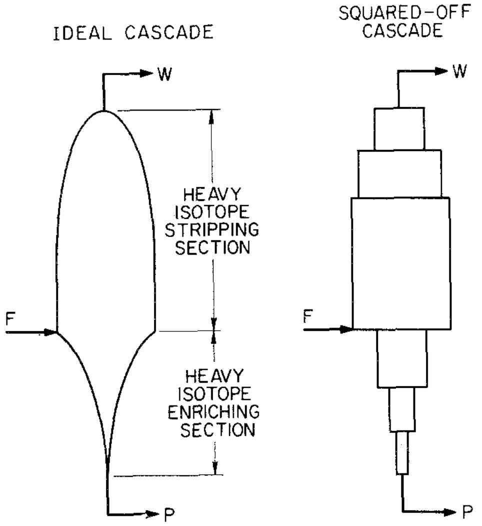

Fig. 8. Comparison of an ideal and a squared-off cascade.

connected in a series arrangement. Fig. 8 shows a schematic comparison of an ideal and a squared-off cascade. The design objective in squaring-off a separation cascade is to approximate the ideal tapered cascade as nearly as possible. This can be accomplished using an equation that will predict the ideal cascade stage composition in conjunction with an equation that will predict the stage compositions and total interstage flow of the squared-off cascade. Because of subtle differences between bipolar cascade design and conventional cascade modelling, it was necessary to derive design equations specifically applicable to a bipolar cascade.

Assume that in a squared-off bipolar electrolysis cascade there are D total square sections with d being any specific square section within the cascade. The square section with $d = 1$ is defined as the final enriching section for the heavier isotope in the cascade. Isotope composition in any section d of the cascade can be expressed as

$$m_{d+1,1} = (m_{d,1}B + C) \sum_{j=0}^{J_d-1} A^j + m_{d,1}A^{J_d} \quad (9)$$

where

$$A = \left(1 - \prod_{k=1}^{d} \rho_k\right) \Big/ \alpha$$

$$B = \rho_d - \left(\rho_d - \prod_{k=1}^{d} \rho_k\right) \Big/ \left(1 - \prod_{k=1}^{d-1} \rho_k\right)$$

$$C = \prod_{k=1}^{d-1} \rho_k m_p \left(\rho_d - \prod_{k=1}^{d} \rho_k\right) \Big/ \left(1 - \prod_{k=1}^{d-1} \rho_k\right)$$

and $\rho_d = L_d/L_{d+1}$, the product-to-feed ratio for square section d, $m_{d+1,1}$ = mole fraction of heavy isotope in stream used as feed for section d, $m_{d,1}$ = mole fraction of heavy isotope in the product stream leaving section d, J_d = total number of stages in section d, and

$$\prod_{k=1}^{d} \rho_k = \rho_1 \rho_2 \ldots \rho_d.$$

Starting from the product end of the squared-off cascade, the feed composition to each square section can be calculated given J_d, ρ_d and α. Derivation of the design equation will be discussed in a subsequent paper and the optimizing technique for a bipolar cascade is discussed in detail elsewhere [29].

One possible application of bipolar electrolytic separation would be the removal of tritium from heavy water used as the moderator-coolant in a nuclear reactor. The objective would be to reduce the tritium content in the coolant to an ultimate equilibrium concentration of approximately one-sixth of its usual steady-state level, e.g., from 20 Ci dm^{-3} to 3.3 Ci dm^{-3}. Simultaneously, it would be desirable to enrich the tritium product to 10 mol%, such that other established enriching methods could be used to eventually obtain pure tritium, a resource of high intrinsic value. The total electrolytic power required for a bipolar squared-off cascade system for this example is approximately 75% of that consumed in normal electrolysis (see [29] for details). The total gas flow, intersectional aqueous flow and the electrolyte recycle rate are reduced to about 25% of those rates required for normal electrolytic separation in an ideal cascade arrangement.

Acknowledgement

This research was sponsored by the Division of Waste Products, Office of Nuclear Waste Management, US Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

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