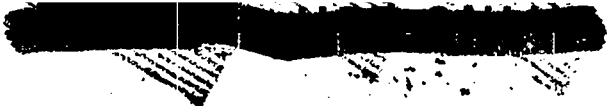


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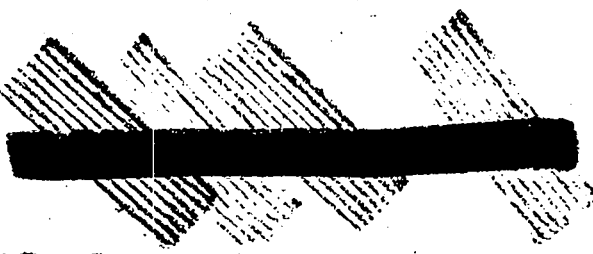
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LITHIUM ISOTOPE SEPARATION BY ELECTROLYSIS

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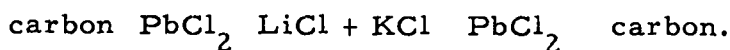
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LITHIUM ISOTOPE SEPARATION BY ELECTROLYSIS

Introduction. A number of experiments concerned with the separation of lithium isotopes are described in the published literature. In the earliest, and actually the largest scale, of these experiments G. N. Lewis and R. T. MacDonald (J. A. C. S. 58, 2519 (1936)) allowed a spray of lithium amalgam droplets to fall down through lithium salt solutions in a 18-meter column. The salt solutions used were LiCl in absolute ethyl alcohol and LiBr in an ethanol-dioxane mixture. The Li^6 was concentrated at the bottom of the column; at or near equilibrium for a counter - current process they obtained Li^6 of about twice the natural abundance. H. C. Urey (J. Chem. Soc. 1947, 562) estimated for this experiment a single stage separation factor $\alpha = 1.025$.

Chemical exchange methods have been tried. T. I. Taylor and H. C. Urey found no isotopic enrichment for the partition of LiBr between water and methylamyl alcohol (J. Chem. Phys. 5, 597 (1937)) and slight fractionation by zeolite exchange (J. Chem. Phys. 6, 429 (1938)).

A. Klemm, H. Hinterberger, and P. Hoernes (Z. Naturforsch. 2a, 245 (1947)) studied the fractionation of isotopes of lithium in fused salt in this cell:



At 630°C , in a tube 0.41 cm inner diameter and 15 cm long, with current density 5 amp. cm^{-2} , after 48 hours they obtained 130 mg of LiCl with $\text{Li}^7/\text{Li}^6 = 44$ (natural value 12.7).

A number of investigators have found a considerable isotopic

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fractionation for the electrolytic deposition of Li^+ ions at a mercury cathode to form lithium amalgam. Taylor and Urey, in papers already referred to, studied the electrolysis of aqueous LiCl and aqueous LiOH ; they give $\alpha = 1.039$ for LiCl at current density $0.62 \text{ amp. cm}^{-2}$. H. L. Johnston and C. A. Hutchison (*J. Chem. Phys.* 8, 869 (1940)) found for LiCl in water or in absolute ethanol $\alpha = 1.055 \pm 0.005$, independent of temperature, of amount of cathode back reaction (in the range of current efficiencies 0.25 to 0.65), and of current density between 0.47 and $0.71 \text{ amp. cm}^{-2}$. Holleck (*Zeits. f. Electrochemie* 44, 111 (1938)) reported for this process $\alpha = 1.079$ at $0.07 \text{ amp. cm}^{-2}$ and 39°C . The difference between these results are more likely in the isotopic analytical methods used than in the experimental conditions.

Oak Ridge National Laboratory reports outline work on lithium isotope separation by exchange reactions, primarily those involving lithium amalgam, and by molecular distillation (ORNL 50-6-161), and by the electromagnetic method (ORNL 50-6-177).

Analysis of the Electrolysis Problem. The survey above suggests that the separation of lithium isotopes by electrolysis very probably would be considerably more economical than the electromagnetic method provided solutions can be found to certain practical problems associated with the design of a simple multistage electrolysis apparatus. If a water solution of lithium salt is the electrolyte provision must be made in the design for a large volume of gas evolved and for the cathodic current inefficiency: ordinarily about 30% of the cathode current goes to produce the net reaction $2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$. If non-aqueous systems are considered the cathode current efficiency can be much

higher than 70% and the gas evolution correspondingly less, but such a system needs to be found and very probably higher electric power costs will result because of the lower specific conductances of non-aqueous electrolytes. Essentially these two approaches have been followed in this research; the non-aqueous systems will be described first although the aqueous systems are now more promising.

Electrolysis in Non-Aqueous Systems at High Cathode Efficiency.

If there were available a practical electrolyte from which lithium could be deposited as amalgam at very high (essentially 100%) cathode efficiency, lithium isotopes could be separated in a vertical column such as is shown schematically in Figure 1. In this column each shallow cup would be made of a metal wet by mercury (probably copper or iron would be satisfactory; surely platinum would) and the amalgam surfaces would be the electrodes - cathode on top and anode on the bottom of each intermediate cup. At each cathode the enrichment of Li^6 would be about 1.05; at each anode the isotope effect is not known but assumption of the factor 1.00 would be indicated. Thus for a single stage (Cell) $\alpha = 1.05$ approximately, and with about 115 cells (115 cups) the product at equilibrium would be 95% Li^6 .

We have sought a suitable electrolyte for this system. Lithium amalgam reacts more slowly with absolute ethanol than with water, but even in this case the cathode efficiency does not approach 100%, and H_2 is evolved. Higher alcohols also react with lithium amalgam though somewhat more slowly. Also specific resistances of lithium chloride or bromide in alcohol are high, of the order of several hundred ohms. Anhydrous ether might be suitable except for the very high resistance

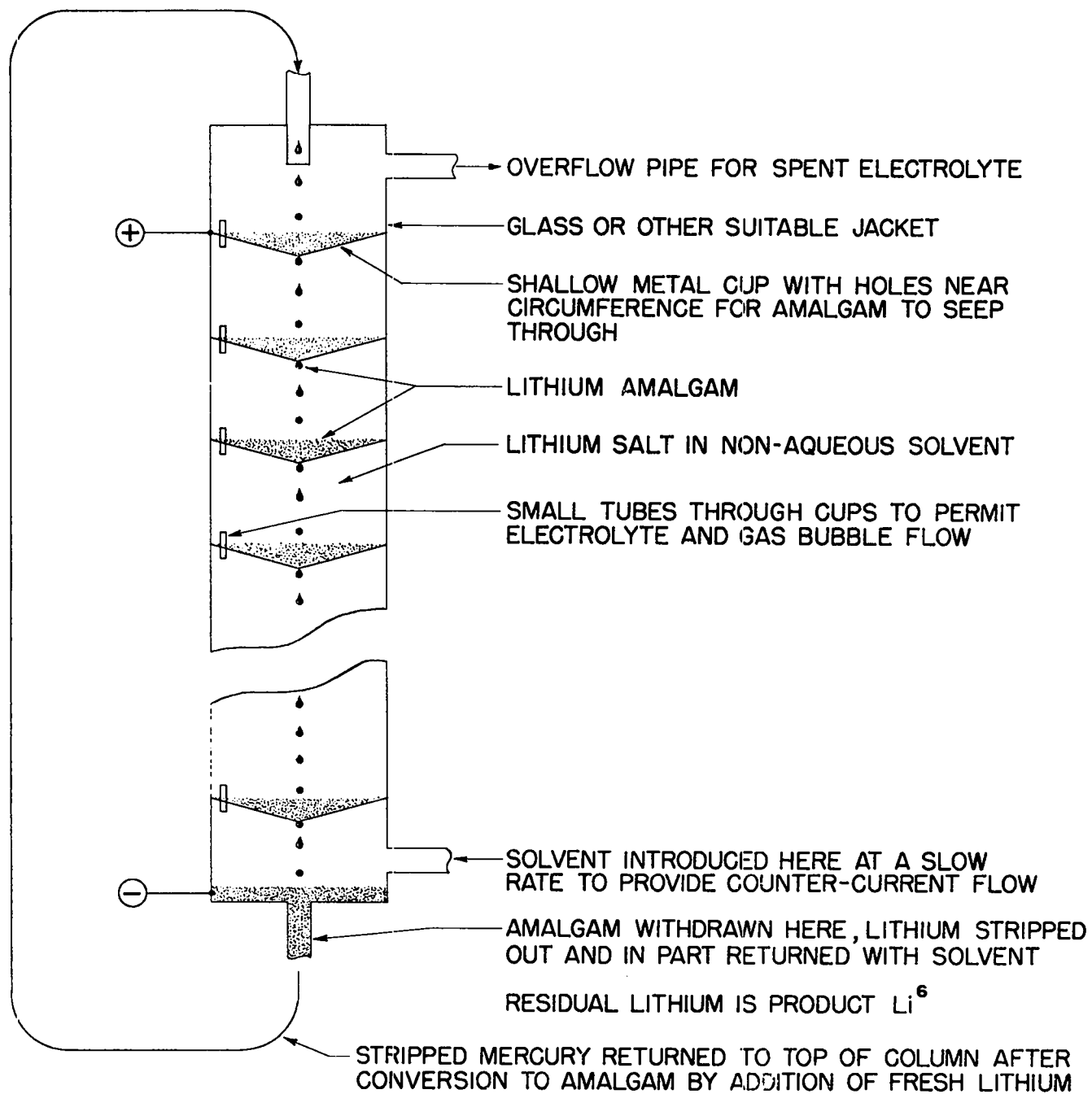
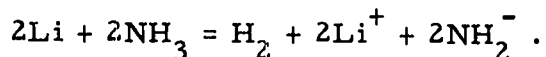


FIG. 1
 VERTICAL COLUMN FOR MULTISTAGE
 ELECTROLYSIS IN NON-AQUEOUS SYSTEM

even of saturated Li I in ether. Pyridine has been used as a conducting solvent for LiCl (Lasczynsky and Gorsky, Zeit. Electrochem. 4, 290 (1897), and Richards and Garrod - Thomas, Z. Physik. Chem. 72, 183 (1910)), but the latter authors note that lithium amalgam reacts slowly with pyridine to give a precipitate after about a day. Liquid ammonia at its boiling point does not oxidize lithium readily, but lithium amalgam is solid at this temperature; at higher temperatures (and pressures) this reaction proceeds:



Lewis and Keyes (J. A. C. S. 35, 340 (1913)) used lithium amalgam electrodes in conjunction with lithium salts dissolved in ethylamine. The boiling point of ethylamine is inconveniently low, 16.6°C, but it dissolves LiCl readily; its dielectric constant is 6.17. The higher aliphatic amines boil higher, but dissolve less salt and have lower dielectric constants and higher viscosities so give much higher specific resistance.

More promise seemed to be offered by ethylenediamine, H₂-N-CH₂-CH₂-NH₂. This amine melts at 8.5°C, boils at 116.1°C, and a relative viscosity of 1.725 (at 25°C). This substance, which we refer to as EDA, is known to be a good ionizing solvent and to be unusually inert toward alkali metals (G. L. Putnam and K. A. Kobe, Trans. Electrochem. Soc. 74, 609 (1938)). We have determined the solubility of Li I in EDA to be 0.9 gram formula weights per liter at room temperature. When Li I is dissolved in EDA there is a large heat evolution, and the subsequent solid phase is certainly Li I · x EDA. The specific resistance of this solution is roughly 50 ohms, which is only two or three times that of a water solution of the same concentration.

We determined that EDA was essentially inert towards lithium amalgam. A sample of amalgam initially 0.114 F was kept under EDA in a glass-stoppered bottle; after four days the concentration was 0.100 F. A sample kept in a similar bottle without EDA after four days was down to 0.031 F.

A final test of the suitability of EDA for this purpose is a test of the "effective cathode efficiency", that is of the fraction of initial amalgam remaining unoxidized after electrolysis from anode to cathode amalgams. In a simple experiment it could only be determined that this efficiency was at least 80 or 90%, because of handling losses and assay error; this was primarily due to the lack of vacuum line facilities for the work. Consequently a cell was set up in which each electrode was 3.5 ml of initially 0.47 F amalgam; the electrolyte was about 10 ml of 0.8 F Li I in EDA. The average current with an impressed emf of 6.2 v was 54 milliamperes. At this current all the lithium at the anode would have been oxidized in 49 minutes. Actually the anode and cathode were reversed at 5 - minute intervals by a time-switch. The cell ran without interruption and with almost negligible gas evolution for 72 hours. The relative amounts of lithium in each amalgam were followed by measurements of the back emf, and crude estimates of the absolute concentration of the amalgams could be made from the change in back emf during the time cycle. After 72 hours the average amalgam concentration (by chemical analysis) was down to 0.20 F, or 41% of the original value. In 72 hours the initial amount of lithium (amalgam) would have been deposited 44 times, so the "effective cathode efficiency" is $100 - \frac{100 - 41}{44} = 98.7\%$. Actually this figure is

a lower limit; some of the amalgam loss must have been due to a trace of water in the electrolyte, though we suspect that about 99% is the true "effective cathode efficiency" for this system, at the current density of 0.017 amp. cm⁻².

The "effective cathode efficiency" determines the rate at which lithium as amalgam must be moved down a given column as the drops shown in figure 1. With the drops almost pure mercury a cell would be working at theoretical efficiency for isotope fractionation. If this is to be the condition at the 100th plate then for 99% "effective cathode efficiency" the mechanical (dropwise) lithium transport will be 100 times the electrical transport at the 1st. cell and this cell will be extremely inefficient for isotope separation. If the worst cell, the 1st. is to be about 50% effective in isotope separation, then a single column may not have more than 50 cells.

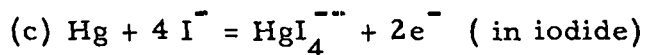
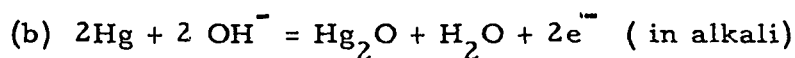
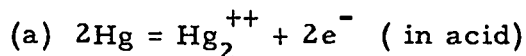
This limitation is troublesome. Also the preparation of anhydrous EDA is not without difficulty. (That used in these experiments was very kindly prepared by Dr. Arthur Murray of the organic chemistry section of group H-4 by distillation over sodium of the Eastman Kodak Co. EDA hydrate.) Possibly some better solvent could be found. Our search of the literature suggested as an alternate type of compound ethylene cyanide (succinonitrile), NC-CH₂-CH₂-CN. This melts at 54.5°C. and boils at 267°C. However when tested in contact with lithium amalgam at 97°C for several days a reaction producing a black tar resulted.

Electrolysis in Aqueous Systems with Anode Depolarizers. The inevitable copious gas evolution in aqueous systems with lithium

amalgam naturally suggests some horizontal geometry for a multiple electrolysis apparatus; in this way gas can be easily vented from an open surface in each cell. An early scheme in our thinking consisted of a linear array of alternate electrolysis and decomposition cells. Amalgam lying on the bottom would flow slowly from cell to cell, the electrolyte would flow slowly in the opposite direction. In each electrolysis cell an inert anode would be used and oxygen would be evolved there. The decomposition cells could use stainless steel pins or grids touching the amalgam and extending into the electrolyte; in this way the hydrogen evolution would be speeded up. Possibly these two functions could be combined into the same physical compartment. There are several disadvantages with such arrangements. They are not economical of space, and in a sense are wasteful of electric power in that the back emf in each stage is more than 2 volts. Also very large currents at very low voltage are required, although possibly several such entire assemblies might be connected in series. Perhaps more serious is the formation of solid lumps of mercury oxide in stagnant amalgam cathodes, presumably by the reaction of mercury with peroxide which has diffused from the anode.

We have tried to find a design that would permit series operation of the successive stages as in the non-aqueous column already described. With a cathode efficiency of about 70% it is essential to provide for a correspondingly low anode efficiency; that is, some reaction other than $\text{Li} = \text{Li}^+ + \text{e}^-$ must also occur at the anodes so that the amalgam concentration does not go quickly to zero. Of course when the lithium in an amalgam anode is exhausted other reactions do

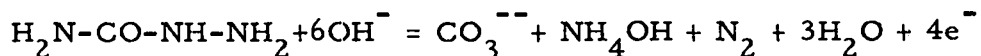
occur:



However, the products of reactions (a) and (c) move to the cathode where they are reduced, so that in a steady state they cannot contribute to maintenance of the amalgam concentration. Reaction (b) consumes the mercury and produces an unwanted precipitate. We have tested some 30 compounds in a search for a suitable anode depolarizer that would not interfere with the deposition of lithium at the cathode, usually in 0.5 F LiOH solution. Most of these reducing agents did not prevent the formation of Hg_2O at the anode; these were glyoxal, oxalic acid, formic acid, pyruvic acid, benzaldehyde, acetylacetone, glycine, p-aminophenol, dimethylformamide, triethanolamine, methyl alcohol, ter-butyl alcohol, α -methylhydroxylamine, hypophosphorous acid, phosphorous acid. The same was true of the following compounds except that they would prevent Hg_2O formation at very low current densities: ethanolamine, diethanolamine, isoamyl carbamate, urea, guanidine, aminoguanidine, dicyandiamidine, dicyandiamide, ethylenediamine, succinonitrile. Some compounds protected the anode mercury but at the same time prevented lithium amalgam formation at the cathode: formaldehyde, hydrazine, hydroxylamine, formamide.

The anode depolarizer that worked well was semicarbazide. This substance (SCA) even in dilute solution in 0.5 F LiOH was oxidized with gas evolution at the anode, and accumulation of Hg_2O was prevented.

To identify the net reaction the volume of anode gas per electric equivalent was measured; it was 0.25 mole of gas. The reduction equivalent per mole of SCA was found by titration against Hg_2O to be very nearly 4 equivalents; in this reaction the gas evolved is very nearly one mole per mole of SCA. All this evidence is consistent with this half-reaction:



Even at 4 equivalents per mole SCA is very expensive for this purpose; unless it could be made in quantity at least one hundred times cheaper than the Eastman Kodak Company retail price (0.03 g.l) it could not be considered. Moreover the byproducts would have to be removed because Li_2CO_3 is only slightly soluble and NH_4OH at high concentrations reacts with lithium amalgam to make first ammonium amalgam and then ammonia and hydrogen.

The other anode depolarizer that worked was sulfur dioxide (present as sulfite ion in the alkaline solution) which was at the anode oxidized to sulfate ion. Commercial SO_2 is sufficiently cheap that cost for this item would not be prohibitive; however the build-up of sulfate ion concentration could present difficulties.

Aqueous Electrolysis without Anode Depolarizers. The difficulties in anode depolarization by chemical means led us to devise a system of electrolysis cells in which anode efficiencies for the reaction $\text{Li} = \text{Li}^+ + \text{e}^-$ can be as small as 70% or smaller without the addition of special reagents. One idea which was tried was this: since lithium amalgam wets metals better than pure mercury, a suitable metal might be covered with lithium amalgam and serve as anode;

when the lithium was exhausted the mercury would fall off and expose the inert metal where oxygen would be liberated by the current. We tried platinum, palladium, copper, tantalum, silver, and graphite. Any of these that were wet by lithium amalgam in the presence of water (all were wet by dry amalgam) were also wet by mercury.

We sought in the literature without success for some liquid amalgam that was sufficiently inert to oxidize water to oxygen as an anode. But we did discover by accident that mercury on copper was only slightly oxidized as an anode, that oxygen was evolved from the passive surface, and that contact with lithium amalgam would renew the bright surface. We built and tried a five-cell electrolysis apparatus based on this principle. There were five rotating copper disks (about 3 inches in diameter) spaced about 1 inch apart on a horizontal, insulating shaft. Each disk as it revolved dipped into a separate pool of mercury. The spaces between the disks were filled with 0.5F LiOH solution. A stainless steel disk (stationary) at one end was made anode and another at the opposite end was made cathode. Thus we had a horizontal analog of the column in figure 1. When a current of 4 amp. was passed, (emf=35v) the mercury in the five pools became lithium amalgam; the steady state concentration was about 0.17 F. However, a suspended green powder, mostly copper oxide, was formed in the electrolyte. Unfortunately this apparatus was destroyed by overheating before it was established that this green powder could not be avoided by suitable choices of current and speed of rotation. Before the apparatus was rebuilt the better scheme described next was devised.

It is possible to make a series of mercury "pools" which serve

with one side as cathode and one side as anode, with an electrical connection from each "pool" to a current dividing network so that roughly 30% of the positive current entering the cathode side does not leave the anode side. Then the operation of the current would be to maintain a steady state concentration of lithium amalgam in each "pool". An analysis of the anode, cathode, and IR voltage drops in the series cells shown that actually an electrical connection from each mercury "pool" to an inert electrode of suitable area immersed in the electrolyte between anode and cathode surfaces of the next except one more negative cell is both satisfactory and economical of electric power. (Of course connection to an even more negative cell of the train could be made to work under proper current and electrode area conditions.) This arrangement is shown in Figure 2. The most negative mercury "pool" cannot be so connected, so is simply connected through a suitable resistor to the cathode terminal to give about the same current "leakage" from this "pool" as from the others.

Figure 2 also shows a simplification of the amalgam surfaces which avoids the rotating copper disks of the earlier model. These disks are now replaced by simple copper screen "barriers" with the screens amalgamated so that mercury fills all the pores of the screens. For this purpose the screen mesh must be very close. Copper plates 0.016 inch thick with No. 51 drill holes on 1/8 inch centers did not work because the lithium amalgam would not fill the holes. Copper screen 80 mesh (80 wires per inch) would retain its pores full of mercury, but with lithium amalgam only the pores within about 1 cm of the bottom edge remained closed. The barrier chosen for further experiments was 100 mesh copper screen divided by horizontal plastic bars (molded

Figure 2

Aqueous electrolysis apparatus with 5 stages and with amalgam barrier electrodes and shield electrodes. Electrolyte is allowed to spill out the overflow near the anode, and enough fresh LiOH is added at "LiOH input" to maintain Li^6 concentration near normal. At the cathode end, water is added and LiOH solution drawn off so as to keep electrolyte concentration constant and give suitable yield of enriched Li^6 .

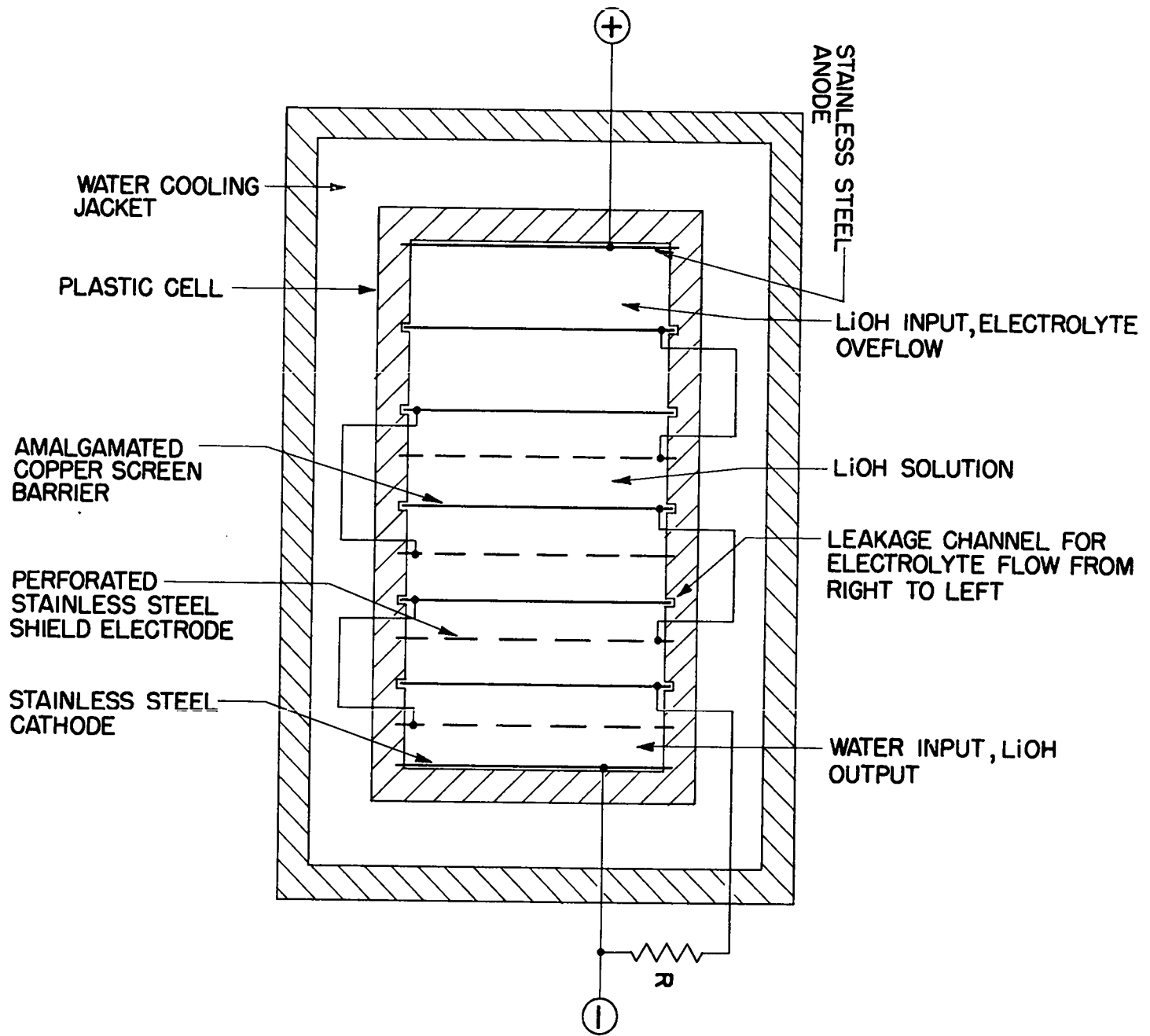


FIG. 2

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on by heat and pressure) into strips only 3/8 inch high.

The "shield" electrodes are made of perforated stainless steel sheet. The electrodes of both types are 2 inches square and are spaced 3/8 inch apart in a plastic box 2 inches wide by 2 5/8 inches deep by 4 1/2 inches long. A water cooling jacket is provided on the outside.

This apparatus works well. The mercury originally in the screen pores becomes bright lithium amalgam at the currents tried, which were 1.0 amp. (12.0volts), 3.0 amp. (15 volts), and 5.0 amp. (17 volts). The amalgam is a lively, mobile liquid which circulates easily and spontaneously through the barrier pores.

An estimate of the cathode efficiency, and thus of the current efficiency of the cells, was made by measuring the current flowing to a typical shield electrode, $i = 0.1$ amp., and comparing this with the total current, $I = 1.0$ amp. Thus cathode efficiency is 90%; under other conditions an estimate of 75% was made.

It might be possible to operate without shield electrodes. One cell so operated developed a heavy green scum on the anode side of the barrier, but the electrolyte there remained clear at least for more than an hour. However the shield electrodes are easily provided and make the cells operate very well without any signs of trouble.

Estimate of Costs. Probably the apparatus just described can be scaled up easily, and more stages added, without any special complications. Better cooling than the simple outer jacket could be in the form of stainless steel internal tubes, which might be so placed and connected as to serve also as the shield electrodes. If the factor per

stage is 1.05 (estimated as before) then about 150 cells might be used. (Because of the changing Li^6 concentration in the electrolyte some cells would be operated further from equilibrium than others.) This many cells would mean a length of about 12 feet. If the cross section were 20 inches by 20 inches, then a current of about 300 amp. (or more) could be passed; the voltage would be about 450v. The lithium would be transported (electrolytically) at the rate of

$$\frac{300 \times 0.866 \times 10^5 \times 7}{96,500} = 1900 \text{ grams per day.}$$

Taking account of the 7.3% abundance of Li^6 and assuming stripping by about 20% of the transport we estimate the rate of production of Li^6 (95% pure) as roughly 30 grams per day for such a unit. The power is about $300 \times 450 \times 1.3 = 1.75 \times 10^5$ watts. The cost of power only per gram of Li^6 produced, at 0.005 per kwh, is roughly 0.70.

Costs other than for power are not so easy to estimate. Cost for supervision for a unit of this size might slightly exceed the power cost, but would trend downward for a larger unit or for several units. Maintenance costs should not exceed power cost. Plant amortization costs can hardly be guessed without some engineering development. The development cost itself is quite uncertain, but might easily be less for this method of separation than for most other methods under investigation.

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