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TECHNOLOGY UTILIZATION

COMMERCIAL POTENTIALS
OF SEMIPERMEABLE MEMBRANES

A REPORT

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COMMERCIAL POTENTIALS OF SEMIPERMEABLE MEMBRANES

A REPORT

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Foreword

One of a series of publications sponsored by the National Aeronautics and Space Administration to make findings resulting from NASA programs available to potential users, this survey deals with advances in membrane technology. It is based on more than 200 reports on NASA-sponsored research, with particular attention given to power sources and life-support systems. Useful references and a bibliography are included to guide the reader interested in further data.

This review is part of a continuing effort to acquaint non-aerospace industry with technological developments growing out of the nation's space program and holding promise for more general industrial application.

GEORGE J. HOWICK
Director, Technology Utilization Division
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CHAPTER 1

New Techniques and Principles

Semipermeable membranes in plants and animals have long interested biologists as well as physical and colloid chemists. Thin barriers which may transport components of a solution selectively are essential to the functioning of living organisms. They have become the subject of extensive laboratory investigation and are being used increasingly in industry. The first such membranes were simple adaptations of naturally occurring polymers: cellulose, gelatin, or animal organs such as the intestines. Later, modifications of these polymers were made utilizing colloidion, cellulose acetate, and rubber.

To develop the devices needed to take men and instruments into space, the National Aeronautics and Space Administration has sponsored research and development of entirely new types of membrane materials. Some of these were previously unknown; others were known, but their properties and limitations had not been explored. This research has been done in response to requirements for unprecedented mechanical properties under environmental conditions of temperature and chemical media far beyond the range considered previously. It was necessary to couple these properties with requisite transport properties both in terms of capacity and in selectivity with respect to gaseous or liquid solution components.

The scientists and engineers responsible for these investigations have had to borrow considerably from polymer science, radiation chemistry, and plastic film manufacturing techniques, even from the biological sciences,

and to apply these disciplines to the problems at hand. Out of their investigations have come new techniques and principles which are potentially capable of stimulating and enriching the science of materials.

NASA projects, for example, have led to development of semipermeable membranes capable of withstanding 30 percent caustic potash at 140° C under oxidizing conditions without suffering degradation or solubilization to any significant degree. It is difficult to find precisely comparable requirements in industry. The long-sought membrane for the production of salt-free caustic and chlorine without the use of mercury may be one such application. Only time and additional research and development can yield the answer.

One purpose of this survey is to call attention to the tremendous advance in membrane technology, not only since Thomas Graham built his classic dialyzer to separate crystalloids from colloids but in the last 5 years. None of the developments described in his summary are included in *Diffusion and Membrane Technology*, American Chemical Society Monograph No. 156, published in 1961, which is a comprehensive summary of the progress in this field to that time.

The newly developed membrane materials are used now only in a few specialty products. There is a timelag between the technical development of new materials and their large-scale commercial development. This lag is caused in part by technological factors and in part by problems of market development and industrial organization. Time

is needed to test and evaluate new and improved products.

A membrane, in the context of this review, is considered to be a medium which separates two fluids, or a solid and a fluid, while permitting a degree of molecular communication between them. The communication may take the form of diffusional, osmotic or electro-osmotic flow of molecules or ions in one direction, or simultaneously in both directions. The distinction between the various modes of molecular transport is not always clearly defined. Always there is a driving force which may be an electrical potential difference, a pressure difference, or a difference in concentration or thermodynamic activity.

The transport is irreversible in all cases and that of each species is limited by a resistance, the reciprocal of which is the diffusivity, permeation constant, or molecular conductivity, depending on whether the driving force is one of concentration difference, pressure, or electrical potential. Despite the irreversibility, the membrane and solutions may attain a state of equilibrium, or near-equilibrium, with respect to one or more of the solution components.

We do not include in the class of membranes the microporous materials in which the transport is largely hydraulic; i.e., involving groups of molecules. Again there are borderline areas in which transport is by a combination of the two modes. The differentiation is defined least sharply where the transport is pressure induced, as in reverse osmosis.

The molecular structure of a membrane is sometimes described in terms of pore size and tortuosity factor, implying a porous structure on a molecular dimensional scale. An alternate model of a membrane as a polymeric network is also sometimes used. The solvent and mobile solute molecules then

are considered to be physically and chemically associated with the polymer. The system is considered to possess all of the properties of a solution, except that the polymer molecules are subject to restraints by forces holding them to the network. Between the points of restraint, the polymer segments are in thermal motion and take part in a segmental diffusion relative to the mobile solvent and solutes.

The latter model is more useful than the other in describing the transport properties of membranes. It describes membrane hydration and imbibition, permselectivity, and many other phenomena important to applications of membranes in the NASA-sponsored programs.

This report will summarize some NASA research and development programs in areas which already have found industrial applications and others which show considerable promise of industrial applications and/or commercialization. It is intended to place these programs in proper technical perspective to enhance industrial utilization of current NASA-developed technology in semipermeable membranes.

Membranes developed as a result of NASA-sponsored research and studies of membrane properties and applications have advanced the state of the art to a point at which important new civilian products and major technological advances should be in the offing. To take utmost advantage of these developments, it is essential that the industrial community be aware of the work that has been accomplished and its technical implications as well as the direction current programs are taking. NASA-developed technology is applicable in areas which are not at once apparent. Even scientists and engineers who are specialists in these areas may not become aware of the real value of the technology without special effort on their part.

CHAPTER 2

Membrane Applications in Batteries

NASA programs are likely to lead to immediate, important, large-scale applications in power sources. Such applications may be in both primary and secondary batteries, in sizes from microminiature to those capable of operating large vehicles or serving as standby power sources. Some of the research efforts may find useful applications in the further development of fuel cells, both large and small.

LEAD STORAGE BATTERIES

The classical lead storage battery now accounts for a large proportion of all secondary electrical power sources in the United States. More than 800 million pounds of lead are used annually for this purpose. Most of the lead batteries are used in automobiles. One battery rated at 50 ampere-hours and 12 volts weighs about 40 pounds, practically all of which is lead. Obviously, a major technological advance will be required to displace the time-honored lead batteries from even a portion of this very large field.

Lead batteries are limited in their resistance to shock, and deteriorate by sulfation when they are idle. In numerous uses their high weight-to-power ratio may be objectionable. Despite these limitations, the lead-storage-battery industry accounts for about one-third of the lead consumption in the United States annually.

The lead battery is subject to considerable improvement by the use of membrane sepa-

rators in place of the porous separators now in general usage. Substitution of membranes may permit a substantial reduction in the space between the plates of each cell and a more compact battery.

NICKEL-CONTAINING BATTERIES

The Edison alkaline battery is more resistant to shock, but is otherwise inferior in performance to the lead-acid battery. A more recent development, the nickel-cadmium (Nicad) battery, has superior ruggedness and reliability. The major items of cost are for cadmium (\$3 per pound) and for producing the plaques of sintered carbonyl nickel.

The requirement for cadmium is from 1.5 to 2 pounds for a 50-ampere-hour, 12-volt battery. The entire annual consumption of cadmium in the United States is only about 12 million pounds, of which 55 percent is for electroplating, 20 percent for pigments, 10 percent for alloys, 7 for chemicals, 5 for plastics, and only 3 percent for other uses including batteries. Replacement of all of the lead-acid batteries would call for some 30 million pounds of cadmium, considerably more than twice the amount now used for all purposes. Cadmium is a byproduct of zinc production and the supply is obviously not adequate for its large-scale use in batteries.

Nicad batteries are being used increasingly, however, in small units for cordless electric appliances, radio and television sets, and flashlights.

NASA SILVER-ZINC BATTERIES

The silver-zinc battery's capacity may be considerably greater for a given size and weight than that of a nickel-cadmium battery. It is, in fact, better in this regard than any secondary battery system that has been developed to date, regardless of cost. This makes it of especial interest in spacecraft applications.

The reliability of silver-zinc batteries is dependent on the properties of the membrane separators. Premature failure may be due to a diffusion of silver compounds through the separator to the negative plate of a cell. It may also be caused by a penetration of the separator by zinc dendrite crystals during the charging cycle. Finally, there may be a tendency of the zinc crystals to slough, i.e., to accumulate near the bottom of the cells, after repeated charge and discharge.

The tendency toward premature failure varies with the duty of the battery; i.e., the rate of charge and discharge, depth at discharge and degree of overcharge, idle time and degree of charge during idling, etc. It is difficult to incorporate the effects of all the conditions of service when specifying laboratory test procedures. These must be set somewhat arbitrarily by establishing a program of charge and discharge to determine the number of cycles before total failure or some arbitrarily selected loss of capacity.

For space applications the batteries must be sealed to contain the gases, mainly hydrogen and oxygen, which are formed at the plates. Fortunately, these gases tend to be consumed, hydrogen at the silver plate, and oxygen at the zinc plate. This recombination limits the pressure buildup and makes possible the construction of a simple and practical battery which requires no maintenance attention to replace the water or electrolyte throughout the working life of the battery.

The cell capacity and the reliability of these batteries are greatly dependent on the quality of the membrane separators. Capac-

ity is affected by the electrical resistance of the separator in the electrolyte, but the reliability is determined only by testing the cell under the conditions of intended service.

The extent to which battery failures are caused by sporadic or random defects, such as pinholes and localized regions of stress concentration or of mechanical weakness, is not known. There are no known nondestructive tests for battery separators. Thus every component of an electronic circuit in a spacecraft may be tested for manufacturing defects prior to assembly, except the battery, the power source necessary for the system to function.

There are perhaps no uses of membranes in which freedom from defects of manufacture are more important than in batteries and in single-membrane fuel cells. In the former the separators are usually applied in multiple layers to reduce to some extent this dependence on perfection. It is also significant that the membranes which have been found to be most satisfactory are those made by modification of cellophane or of polyethylene film, both of which are produced commercially under rigid quality control.

There are dimensional changes when membrane separators become wet with the battery electrolyte. With cellulosic materials there is a shrinkage in lateral dimensions which accompanies a swelling in the dimension of thickness. Separators made by radiation grafting tend to expand laterally while undergoing a shrinkage in thickness. This is ascribed to the orientation of the grafted polymer chains in the direction perpendicular to the faces, whereas the cellulose molecules in cellophane tend to orient in the direction of drawing of the film.

This means that the plates should be wrapped with due regard to the dimensional changes which ensue and, furthermore, that this should be done differently for the various separator materials. NASA studies have demonstrated that failure to take this factor into account may lead to erroneous conclusions relative to a comparison of membrane

performance, and that optimum battery performance is obtainable only by use of appropriate wrapping methods.

Studies are in progress to determine methods to avoid wrapping of electrodes. One such method (ref. 1) is to coat electrodes with polymers. Another method is to electrodeposit calcium and magnesium hydroxide on the silver electrode.

Silver-zinc batteries, development of which has been very considerably assisted by NASA-developed technology, should be competitive commercially with Nicad batteries. To balance the increased cost of the metal to fabricate the silver plates, there is a 50-percent increase in cell voltage and a saving in cadmium and nickel plate fabrication cost. Nicad batteries may employ separators, but are not totally dependent on them. Silver-zinc batteries, on the other hand, are possible only with the use of separators.

Development of such separators has been one of the most important aspects of NASA technological efforts in the battery field. These efforts still continue because of ever-increasing requirements for improved separators capable of withstanding extremes of temperature, chemical environment, and heavy rates of charge and/or discharge over long periods of time and over many cycles. (See ch. 3.)

A HEAT-STERILIZABLE BATTERY

Highly important developments have resulted from the effort to satisfy Jet Propulsion Laboratory requirements for a battery to withstand repeated heat sterilization at 145° C. To do so in the presence of the potassium hydroxide electrolyte, a separator must possess an unusual degree of chemical resistance while maintaining its ability to conduct an ionic current to the extent required.

Lander and Bogner (ref. 2) found that certain radiation-grafted polymer films resisted the thermal and chemical attack sufficiently to retain some of the mechanical and

electrochemical properties. Relatively small amounts of soluble products of decomposition resulting from combined chemical and thermal attack were thought, however, to poison the silver plates seriously, resulting in loss of capacity. Later effort by Sartwell (ref. 3) led to development of improved separator materials which not only resist thermal attack upon their physical integrity but which are not subject to the tendency to cause formation of deleterious products which might impair the performance of the plates. This effort is being continued (ref. 4).

In the course of study of the resistance of various materials to 40 percent caustic potash at 145° C, it was found that radiation-grafted acrylic Teflon, methacrylic Teflon, sulfonated styrene Teflon, Dynel, nylon, and Zytel 38, 101, 121 all were attacked to a degree, some greater than others. In some cases the attack was evident from the change in physical appearance or properties. However, even when there was no evidence of physical deterioration, effects were noted which might indicate, subject to confirmation, that the decomposition products in the electrolyte might have affected adversely the performance of the cells.

Cells with six positive and seven negative plates were discharged at a standard rate of 9 amperes. Nominal capacity of the cells was 25 ampere-hours. Typical discharge curves are given in figure 1 for Zytel 38, Dynel, Penton, and fibrous sausage casing FSC (cellulose), as well as for a control consisting of one layer of Dynel and three layers of fibrous sausage casing. After full-capacity discharge, the cells were recharged and cycled until failure.

In other test series performed under somewhat different conditions designed to evaluate resistance to heat sterilization, discharge curves of cells using radiation-grafted Teflon and crosslinked high-density polyethylene were obtained. These are shown in figure 2 for both the heat-sterilized and unsterilized (control) cells. From a com-

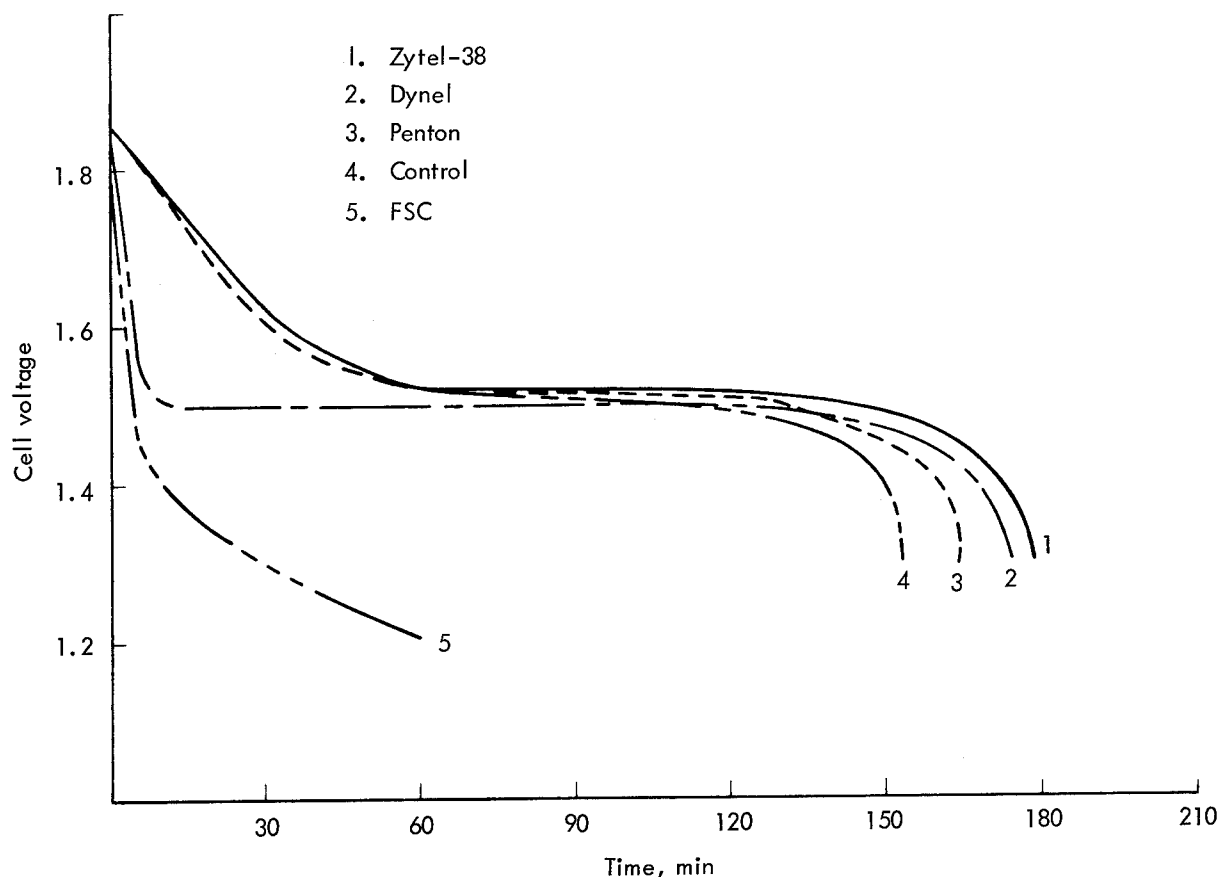


FIGURE 1.—Typical discharge curves at 9 amperes. Each group is average of three cells.

parison of the performance as shown, there is actually a benefit of the heat treatment from the standpoint of capacity in the earlier cycles. This is shown to a lesser extent in the curves of figure 3 for other radiation-grafted modifications.

However, as shown in table I, these sterilized cells with modified Teflon tend to lose capacity sooner, after prolonged cycling, than the controls. Ultimately, there is a failure due either to plate deterioration or to shorting as noted in the table. Soluble degradation products are believed by some to be responsible. It is of interest to note that the polyethylene-based membranes are better in resisting the sterilization than those derived from Teflon, because exposure to radiation tends to promote degradation of Teflon, while in polyethylene it tends more toward crosslinking. Exposure to hot caustic

tends to leach the lower molecular weight components and leave a matrix of very high permeability compared to that of unirradiated Teflon.

With high-density polyethylene the performance is much better from the standpoint of cycle life following sterilization. The difficulty with the radiation grafting is due probably to the difficulty of obtaining grafting uniformly through the membrane with crosslinking limiting the degree of swelling and penetration of the monomer in the grafting process. More recent developments have tended to indicate that this problem has been largely overcome.

The result has been the development of a membrane which is not only resistant to heat sterilization but is superior in its re-

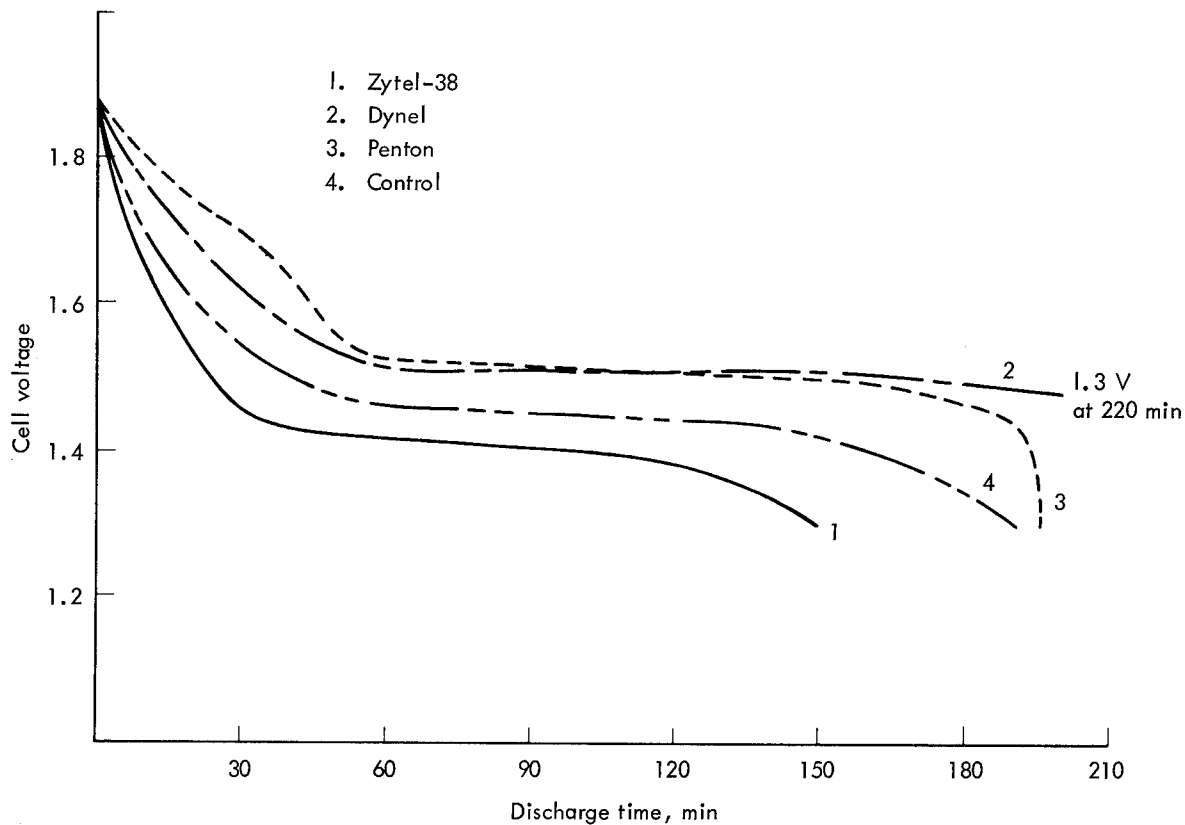


FIGURE 2.—Discharge curves of cells built with Radiation Applications, Inc., (RAI), separators (9 amperes at room temperature 2d cycle).

TABLE I—Cycle and Capacity Data—Cells With Radiation Applications Inc., Separators
[In ampere-hours]

Cycles	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
AA ^a on Teflon control	29.6	28.6	27.3	27.7	22.5	24.9	24.9	23		19.2	18.5	18	7.3	9	2
AA ^a on Teflon sterilized	30.8	Removed from test—shorted Oct. 7, 1963													
AA ^a on Xlhdpe ^b control	19.4	19.6	19.5	18.5	18	19.2	18	14.8	17	16.5	13.5	14.4	14.4		
AA ^a on Xlhdpe ^b sterilized	22.2	22.2	21.4	20.1	21.4	19.2	18	16.1	17.4	17.7	17.4	19	17.1		
MAA ^c on Xlhdpe ^b control	22.3	24.2	23.6	21.6	22.5	23	22.5	19.1	19.5	21.2	20.6	21.4	19.6		
MAA ^c on Xlhdpe ^b sterilized	30.7	31	30.7	30.7	31.5	31.5	27	30.1	31.5	31.2	31.3	26.8	30.8		
MAA ^c on Teflon control	24.9	5.2	Removed from test, Oct. 23, 1963												
MAA ^c on Teflon sterilized	Removed from test														
Sulfonated styrene-Teflon	22.5	23.6	23.4	21.6	21.4	21	20.4	18.6	19.1	19.7	18.4	19.5	17.6		

^a AA—acrylic acid.

^b Xlhdpe—cross-linked identity polyethylene.

^c MAA—methacrylic acid.

sistance to dendrite penetration and other causes of failure. These membranes are only 1 mil thick. Using three layers for the sepa-

erator, it becomes possible to combine long life with the highest possible energy output and storage capacity per unit of size or weight.

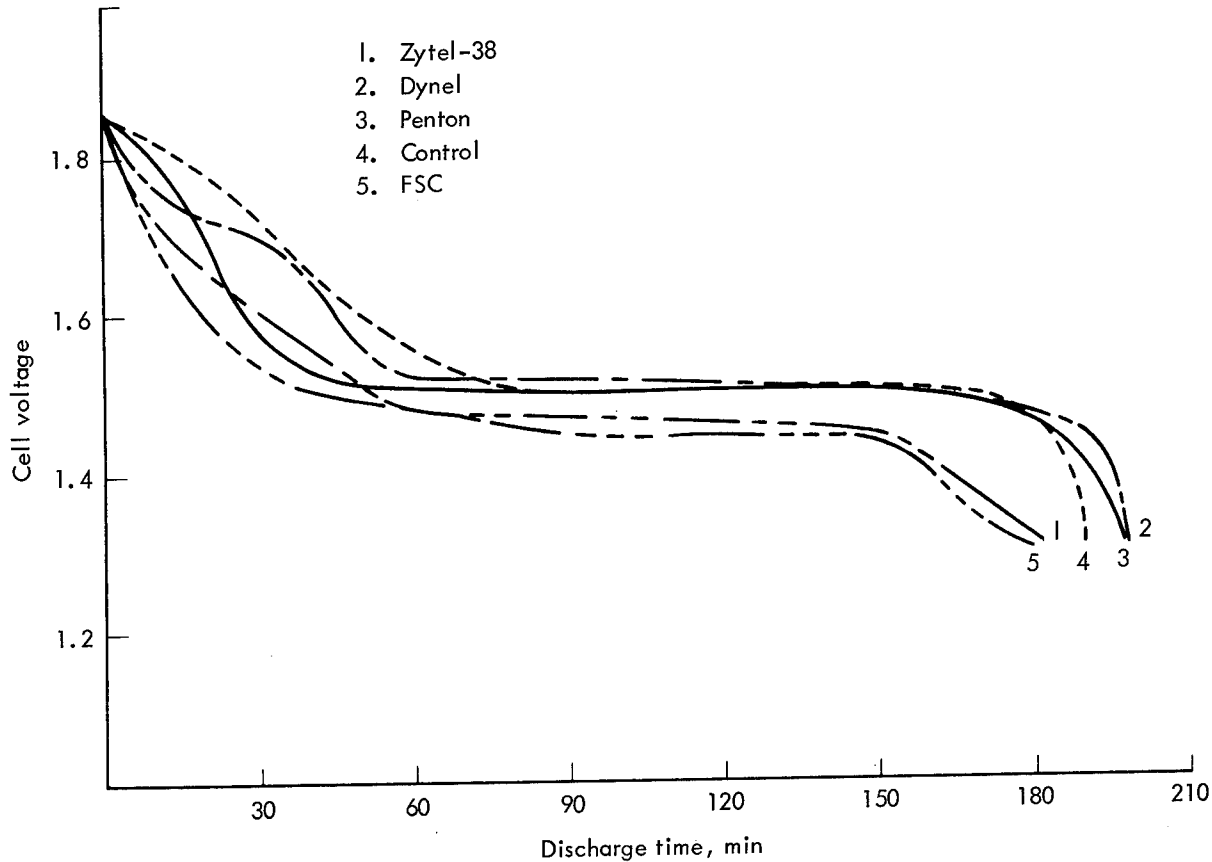


FIGURE 3.—Discharge curves of cells built with RAI separators (9 amperes at room temperature 2d cycle).

NICKEL-ZINC BATTERIES

The greatest impetus to advances in the technology of secondary batteries is likely to come from development of a nickel-zinc system to replace the Nicad battery.

The nickel-zinc battery has never been developed, either vented or sealed, to a degree which would indicate promise of ultimate commercial success, but several companies are working on this problem at this writing. The most recent NASA efforts (ref. 3) make it appear quite probable that the separators, or modifications thereof, developed for the silver-zinc batteries may be applicable as well to a commercially feasible nickel-zinc system. For this system, the requirements for prevention of zinc dendrite penetration are the same as, and possibly

more severe than, for the silver-zinc. Additional problems may arise from the effect of alkali zincate upon the performance of the nickel plate.

Improvements in the nickel plate are not properly within the scope of this report, but it should be noted that plate construction and separator material design are related, inasmuch as each plays an important role in the performance of the other. For example, the soluble products of separator material may have a profound effect upon the rate of combination of hydrogen and oxygen in sealed batteries. This was shown by Charkey and Dalin (ref. 5) by tests of silver-cadmium batteries indicating that soluble products of separator materials tended to lower the rate of oxygen combination by a

factor of 2.5. Although the chemical nature of decomposition is not known, the products are formed by oxidation of cellophane by silver oxide in the 30-percent potassium hydroxide electrolyte. Other decomposition products of a deleterious nature are formed when separators of polyvinyl alcohol and radiation-grafted polymer membranes are used.

The successful commercial development of a nickel-zinc battery, assisted by NASA separator development achievements, could have a very important impact upon the growth of the secondary battery industry for portable radios and television sets, portable power tools, etc. As in the case of the silver-zinc battery, the separator is the most critical component.

If it should be found possible to reduce the cost of fabricating the nickel plates, it is conceivable that use of this battery could be extended to the automotive field and to electrically propelled vehicles. The nickel-zinc batteries are about 40 percent higher in voltage output than the Nicad and there is a saving in cadmium.

NASA-developed technology of separators may be applicable to the development of a nickel plate which is more reasonable in cost and comparable in performance to the sintered plates now in use. The problem is one of containing the hydrated nickel compounds which are the active components of the plate. These compounds undergo a considerable dimensional change during charge and discharge, and a means is needed of containing them while providing electronic conduction sufficient to have the required plate capacity at the desired rate of charge and discharge. One possibility is to provide a structure composed of an electrically conductive elastomer within which the active nickel compound may be formed. The plate material, of course, would have to possess the same properties of chemical resistance as are required for the separator. Technology related to the development of the separator mate-

rials is, therefore, in part at least, applicable to this problem.

NASA-developed membrane technology may contribute greatly to advances in primary as well as secondary power sources. It is very likely that the advances in secondary power sources may ultimately limit the use of primary batteries to areas now served by the common expendable dry cells and special units. The latter may be expendable batteries designed for applications which require the ultimate in compactness and flexibility as a means of obtaining a very rapid discharge of energy. It is reasonable to expect that some of the NASA research not specifically aimed at primary battery development may be applicable.

PRIMARY BATTERIES

An example of a primary battery developed as an offshoot of a research effort aimed at another target is a dry-tape battery developed by Gruber, Borsanyi, Kafesjian, and Smith (ref. 6). This battery was designed to demonstrate the feasibility of producing electrical energy on demand and it involved technology which is readily applicable to the design of extremely compact primary batteries. In this system, silver peroxide is coated on a tape of fabric using a binder to hold the particles to the base material. (See figures 4-7.) Another tape carries a solution of potassium hydroxide and a zinc sheet constitutes the negative electrode. A primary battery formulated in accordance with this principle might be designed having nearly infinite shelf life with activation provided merely by pressing the components together into contact. It should promote a discharge current density of 150-amps per square foot with 85 percent utilization of the silver peroxide. A separator material may be of the order of no more than 1 mil in thickness and the entire assembly should be nearly the ultimate in compactness.

A project to obtain design data to make possible the construction of a reliable primary silver-zinc battery having satisfactory voltage control, charge potential character-

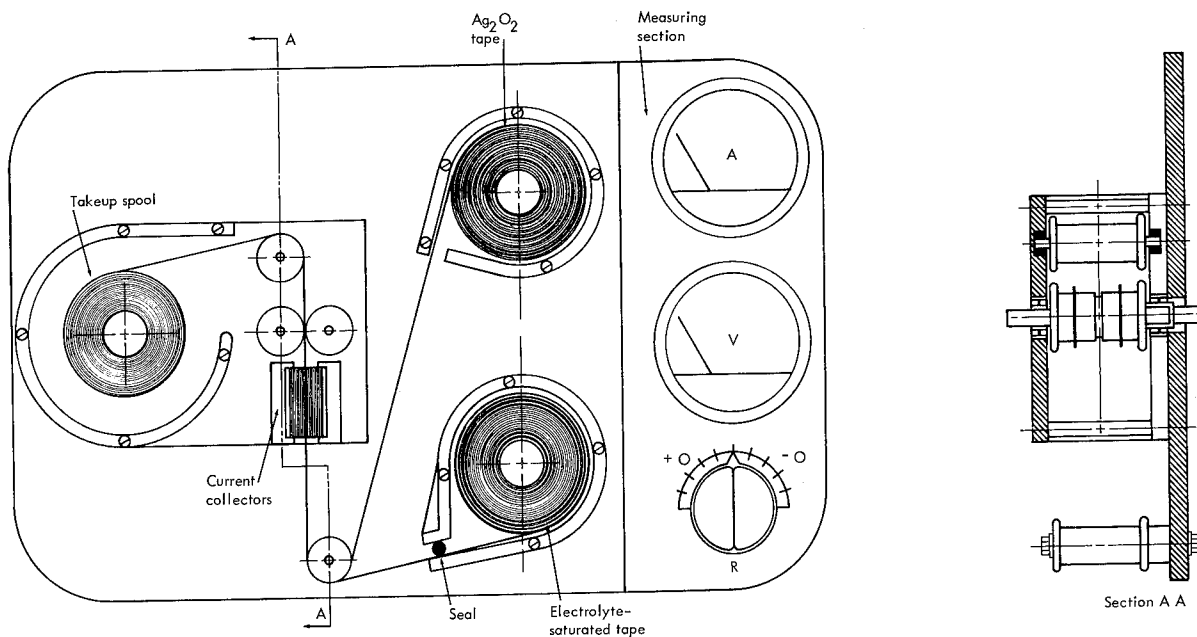


FIGURE 4.—Tape deck assembly of prototype demonstration battery.

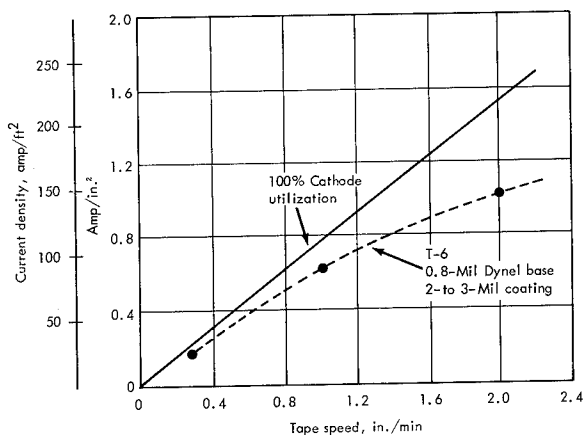


FIGURE 5.—Effect of tape speed and current density on cathode utilization, tape T-6.

istics, energy density, temperature stability, and a minimum of gas was undertaken by Hawkins (ref. 7). The separator materials included in this study were of cellulose, radiation-grafted polyethylene, and microporous polyethylene. Properties which were studied included resistivity, speed of wetting, silver migration, retention of charge, and absorptivity. Included in the study were the effect of electrolyte concentration and the effects of various additives.

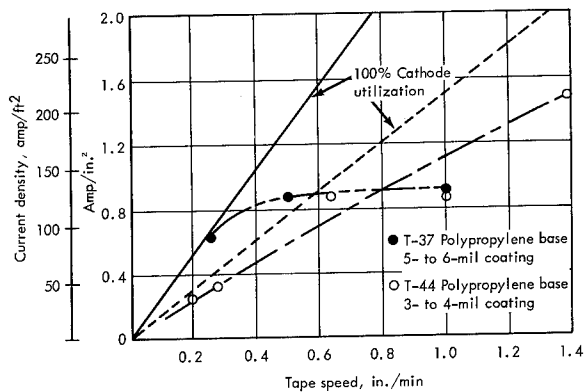


FIGURE 6.—Effect of tape speed and current density on cathode utilization, tapes T-37 and T-44.

TRENDS

The early period of secondary battery research saw the development of the lead-acid battery and the Edison nickel-iron battery. They require no separators of the membrane type, although they may, in the case of acid batteries, utilize thin cedar wood or, more recently, microporous plastics to permit a very close spacing of the plates without shorting.

Lead-acid batteries, still the mainstay of automotive starting systems, are also used

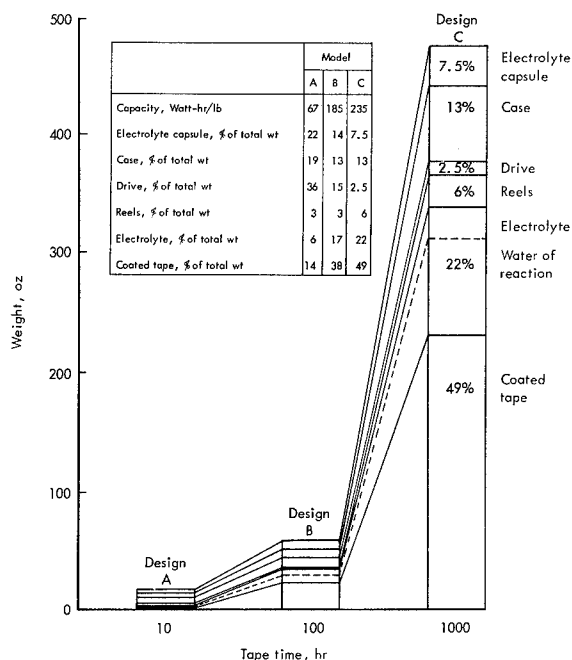


FIGURE 7.—Projected energy densities for magnesium/m-dinitrobenzene dry-tape fuel cells. The weight in ounces and the capacity in watt-hours/pound are indicated for three typical battery design capacities. Tape feed, 1 in./min. Current, 5 amp. Couple, m-DNB/mg.

for storage of emergency power in stationary, marine, and railroad installations. The Edison alkaline battery has achieved an established market based on its mechanical ruggedness. Nicad batteries, with their greater energy output, have established a position in specialty and military applications.

These battery systems are difficult to surpass from the standpoint of capacity or output per dollar of cost. NASA requirements of maximum capacity and output rate, however, have directed attention to development of newer systems. Silver-cadmium batteries utilize membrane separators, although they are not of critical importance. Silver-cadmium batteries are therefore an excellent means of testing separators for migration of silver inasmuch as the problem of cadmium growths is a very minor factor in the shorting of the cells. On the other hand, the silver-zinc system is critically dependent on the

performance of the separators and much of the development effort has involved the formulation, production, and testing of these separators. Silver-cadmium batteries, it may be noted, have been of critical importance to the space program as the only secondary nonmagnetic batteries for flights such as Explorer, IMP, and OGO.

Although cellulosic separators are subject to oxidation and degradation in alkaline electrolytes, it has been difficult to develop synthetic materials with better characteristics. Cellulose retards the diffusion of silver compounds from the positive plate and the penetration of zinc dendrites from the negative. It imposes a comparatively small amount of electrical resistance in the battery circuit.

Some success has been achieved in improving cellophane by various chemical modifications. Nevertheless it appears likely from NASA studies that cellulose eventually will be replaced in separators by polyethylene modified by radiation grafting. Some materials have shown outstanding resistance to strong alkali at elevated temperatures, and appear to resist shorting from all causes over many cycles of battery charge and discharge.

The commercial development of silver-zinc batteries will be limited because of the high cost of the silver. However, it does not appear likely that the same separators which offer promise of improving the performance of silver-zinc batteries will make possible the development of nickel-zinc batteries, which offer much opportunity for widespread expansion of alkaline battery usefulness. NASA studies have contributed to an understanding of mass transfer across membranes and the effect of membrane decomposition products on battery-plate performance.

The dry-tape battery is an interesting and potentially important development in primary batteries. This system is sometimes classified with fuel cells inasmuch as the battery continues to generate energy as long

as the tape containing silver oxide continues to run through the battery. The zinc electrode, however, must be replaced periodically.

CHAPTER 3

Advances in Material Science

Stringent membrane requirements have led to advances in polymer chemistry of membrane material development that will have far-reaching effects, if fully appreciated, not only for power sources but in other applications, some of which may be difficult even to envision at this time.

RADIATION GRAFTING OF POLYMERS

Techniques of modifications of polymers by radiation grafting are especially intriguing. As applied to the formulation of battery separators in NASA-sponsored investigations, this is typically done as follows:

A polymer film is exposed to radiation in the presence of solution of a polyfunctional monomer in an organic solvent which is substantially unaffected by the radiation exposure. The radiation may cause formation of a free radical by the splitting off of hydrogen or a substituent on the polymer composing the film. Depending on the nature of the polymer, radiation intensity and duration, temperature, and other factors, several possibilities exist. First, it is possible for the hydrogen atoms or protons to recombine with the free radical and restore the polymer to its original condition. Other possibilities include rupturing of the polymer chain, crosslinking with another adjacent polymer chain, or grafting by addition of monomer molecules.

In NASA-sponsored investigations these techniques were used for the modification of polymer films to obtain desired membrane properties. The same, or comparable, techniques are applicable to the modification of

the surface properties of constructional plastics; e.g., to obtain bonding with adhesives or coatings, to obtain antistatic properties, or for metalizing.

In a similar manner, fibers of such material as polypropylene may be treated by radiation grafting using techniques developed in NASA-sponsored work to permit dyeing with all types of dyes. In such applications the technique permits penetration to a depth of only about 10 mils from the outer surface. In many typical cases the technique involves a posttreatment of the grafted layer, e.g., by sulfonation, quaternization, etc., to obtain the desired structure and properties.

These investigations have yielded considerable insight into the effects of radiation on polymers of various kinds in terms of the free radical reactions which are the result of radiolysis. Much remains to be done to obtain specific reaction rates of recombination, polymer splitting, crosslinking, graft polymerization, and branching and termination. The principles derivable from these data are applicable to polymer reactions induced by chemical catalysis, homogeneous or heterogeneous, as well as to the reactions which are radiation induced. The latter, however, which have been used most extensively for the crosslinking of polyolefins and for graft polymerization in producing membranes having specialized transport properties, are much more versatile with regard to free radical reaction control. To study and measure the rates of the component reactions is therefore easier.

Radiation also makes possible the halogenation of polymers without the degradation which normally accompanies the aliphatic halogen substitution. At the temperatures required for chemically induced halogenation, side reactions always occur to a significant extent. Radiation-induced halogenation usually proceeds more smoothly. Evidence of this is available in the bromination of hydrocarbons, a process now conducted on a commercial scale.

For the crosslinking of polymers, various methods are available, largely as a result of NASA-supported investigations. Radiation alone suffices to crosslink polyethylene. Polymers such as cellulose require a more involved treatment, consisting of the grafting of styrene and divinyl benzene with post-curing to develop the required crosslinking. This treatment improves the chemical resistance of cellulosic materials such as cellophane.

RESISTANCE TO EXTREME ENVIRONMENTAL CONDITIONS

In the silver-zinc battery system, the separators must resist not only temperature and chemical attack but also the penetration by the zinc dendrites into the diffusion of silver. With this combination of requisite properties, it should become feasible at last to produce batteries which could withstand many cycles of charge and discharge under extreme conditions. Such batteries, vented or sealed, could be used as a very compact power source in various sizes and capacities. NASA programs have been devoted to the design of such batteries for many types of cycling conditions, from rapid charge, slow discharge to slow charge, rapid discharge. Silver-zinc cells may be used in many of the smaller civilian applications for which the cost of silver is no obstacle to its use.

The separators, which were developed to resist extreme environmental conditions, were also found to provide a basis for a greatly improved battery from the standpoint of reliability and the ability to withstand long cyclic periods. Lander and Keralla

(ref. 8) found that a three-ply separator, 3 mils in total thickness, was able to withstand more than 2500 cycles involving a 50-percent capacity drain. This opens new vistas for extremely compact power sources capable of withstanding the most severe conditions of exposure and service.

This most recent development is actually the culmination of NASA efforts over several years. Much effort has gone into improving cellulosic separators by selection from among the numerous commercially available materials, as well as by chemical or physical modifications of materials, to render them more effective as separator materials.

As an example of such effort, screening tests by Oberholzer, Ockerman, and Weiss (ref. 9) have been made upon cellophane, alone and impregnated with silver and anti-oxidants. These tests were used to determine chemical and environmental resistance to hydrolytic action and oxidation; mechanical properties; tensile strength and dimensional changes in the electrolyte; electrolyte absorption and retention; porosity and tortuosity; permeability and reactivity to silver ions; and resistance to zinc dendrite penetration.

Together with the cellulosic materials, the evaluations covered microporous plastics, alone and impregnated; acrylic and methacrylic polymers, and copolymers; radiation-grafted carboxylic monomers on polyethylene and Teflon; polystyrene crosslinked homopolymer derivatives; and heterogeneous membranes. Cellulosic membranes were found best in their resistance to silver diffusion, but suffered from chemical attack. All the methods of achieving structural or chemical reinforcement led to a reduction of conductivity. Resistance to zinc dendrite penetration increases with the separator thickness and is best for the heavier cellulosic materials, e.g., sausage casing, on the basis of resistance-per-ply layer. Other materials are superior to regenerated cellulose on the basis of resistance-per-mil thickness.

Any material which is subject to delamination suffers in its resistance to penetration.

The Oberholzer, Ockerman, and Weiss report includes a comprehensive summary of data pertaining to the properties of a considerable number of separator materials which have been used or proposed for zinc-silver oxide batteries. These properties include tensile strength determinations and results of accelerated aging in battery electrolyte, absorption and retention, silver reactivity and diffusion, and resistance to zinc dendrite growth.

Preliminary evaluation indicated considerable promise for separators formulated by copolymerization of methacrylic acid and vinyl alcohol. None of these showed the high reactivity with silver which characterizes cellophane. However, figure 8 shows some differences indicated by the reduction in conductivity with time of reaction. An increase in degree of crosslinking also causes a drop in silver reactivity, but the result is

less pronounced than the effect of changing the monomer ratios.

Other potentially useful separator materials were studied by Hoyt and Pfluger (ref. 10). These materials included hydroxyethyl cellulose, polyvinyl alcohol and some hydroxyethyl polyvinyl alcohol types. These are materials which are soluble in water or dilute solutions, but insoluble in 30 to 40 percent potassium hydroxide solutions. Membranes made of these materials showed higher capacity than cellophane at a 50-ampere discharge rate for a cell of six silver oxide and seven zinc plates, 1.75 by 2.125 inches. Some of the separator materials have improved resistance to oxidation compared with cellophane and show promise of potentially better performance in life-cycling tests.

One of the conclusions to be drawn from the extensive work of NASA and the armed services on silver, zinc, and other battery

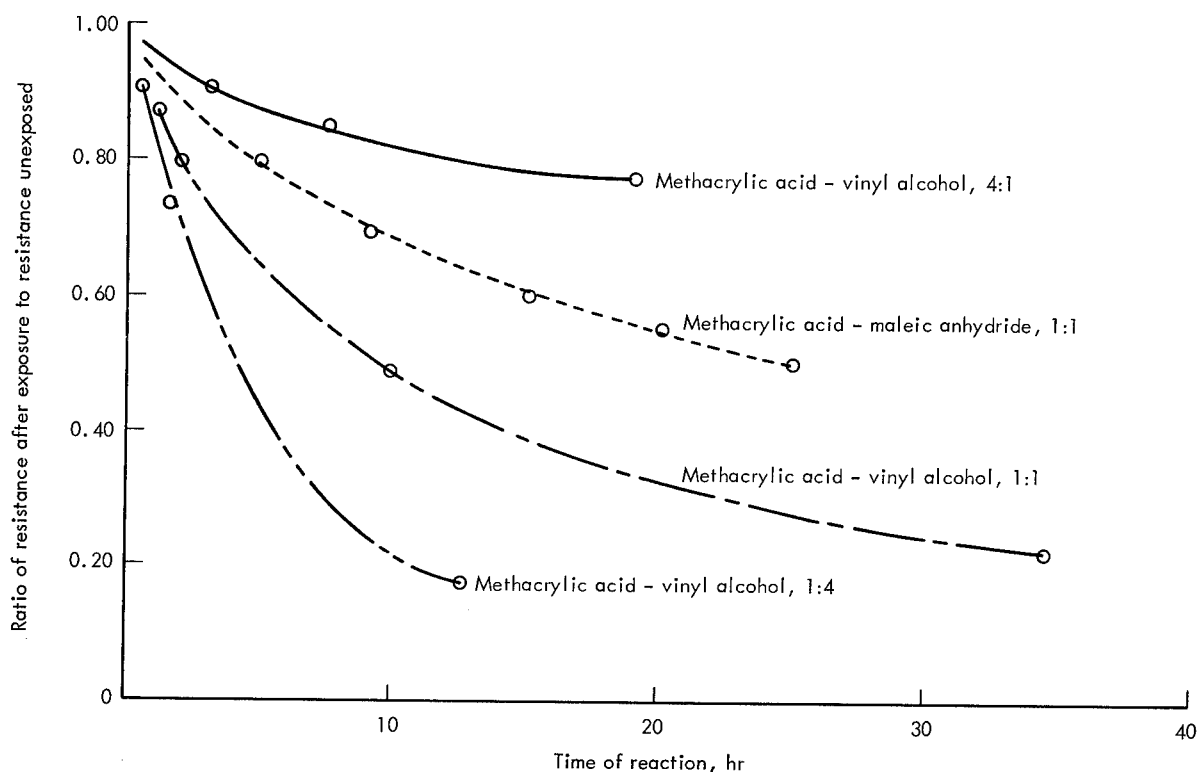


FIGURE 8.—Ag reaction of ion-exchange copolymers.

systems is that no single combination of plates and separators is ideal under all service conditions. A battery subject to very slow charge and discharge may have to be quite different in construction from one which is required to discharge rapidly; and this in turn may be quite different from one which is required to take a fast charge. If the charge and discharge rates are slow, the separator may have a rather high electrical resistance without undue penalty. One means

of controlling the permeable rates of charge and discharge in sealed batteries is by control of the electrolyte level on the two sides of the separator. This was investigated by Hartman, Cushing, and Chreitzberg (ref. 11) in a study of factors of separator composition affecting the tendency of the level to rise or fall with passage of current. Methods were also investigated for obtaining automatic control of the level under operating conditions to optimize each system.

CHAPTER 4

Level Control in Batteries

Goddard Space Flight Center has been interested in means of controlling the electrolyte level in nickel-cadmium and silver-zinc cells (ref. 11). The achievement of level control was attempted with bellows and polyethylene pillows. Level control is quite important in its effects upon the recombination rates of gases produced in charging and upon the plate capacities on charge and discharge.

The purpose of this work was to study the advantages gained by operating sealed electrochemical cells in the flooded condition, while at the same time allowing a provision to depress the electrolyte level to facilitate the recombination of gases in the cell when required. In conventional sealed cells the amount of electrolyte is limited; i.e., the level is maintained at about one-fourth of that which corresponds with the flooded condition. Poor wicking ability of the separator material together with a tendency of the electrolyte to transfer across the separator during charge and discharge leads to highly adverse effects of gas pressure and loss of capacity. Goddard has developed methods of charge control for both large and small cells that allow the cells to be nearly flooded.

EFFECT OF CHARGE AND DISCHARGE RATE

The electro-osmotic effects create a rise in electrolyte level in the negative-plate compartment on charge and a corresponding decrease in level in the positive-plate compartment. A corresponding level change in the opposite direction occurs during discharge.

To obtain a measure of this effect, 12

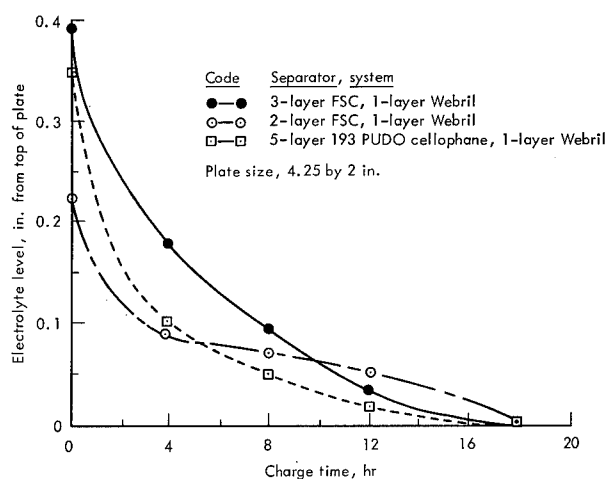


FIGURE 9.—Electrolyte level variation during charge of sealed 15 ampere-hours Ag-Cd cells.

sealed silver-cadmium cells were charged at 0.70 ampere (10 ma/sq in.) to 1.55 volt. Figure 9 shows the average variation in electrolyte level in going from a condition of 70 percent discharge to a full charge for three separator systems. The concentration and level changes that occur in the three alkaline battery systems are summarized in table II.

The investigators in the Goddard study assumed that the changes in electrolyte level from one to the other side of the separators were due to concentration differences in the electrolyte, resulting in osmotic effects. There is some real doubt about the validity of this assumption of the cause of the changes in the electrolyte level with charge and discharge of the batteries. The level change is an electro-osmotic phenomenon, although the osmotic-pressure difference

TABLE II—Concentration and Level Changes in Electrolyte During Charge and Discharge^a

Reaction in positive-plate compartment during charge	Reaction in negative-plate compartment during charge	Net change in electrolyte level	
		Positive compartment	Negative compartment
System: Cd/KOH/NiOOH On nickelic oxide plates: $2 \text{Ni}(\text{OH})_2 + 2\text{OH}^- \rightarrow 2 \text{NiOOH} + 2\text{H}_2\text{O} + 2e$ [OH ⁻] falls during charge. [HOH] rises during charge.	On cadmium plates: ^b $\text{CdO} + \text{H}_2\text{O} + 2e \rightarrow \text{Cd} + 2\text{OH}^-$ [OH ⁻] rises during charge. [HOH] falls during charge.	No change. No membrane to create osmotic effect.	No change. No membrane to create osmotic effect.
System: Cd/KOH/AgO On AgO plates: $\text{Ag} + 2\text{OH}^- \rightarrow \text{AgO} + \text{H}_2\text{O} + 2e$ [OH ⁻] falls during charge. [HOH] rises during charge.	On cadmium plates: ^b $\text{CdO} + \text{H}_2\text{O} + 2e \rightarrow \text{Cd} + 2\text{OH}^-$ [OH ⁻] rises during charge. [HOH] falls during charge.	Membrane present. Water transferred out. <i>Electrolyte level falls.</i>	Membrane present. Water transferred in. <i>Electrolyte level rises.</i>
System: Zn/KOH/AgO On AgO plates: $\text{Ag} + 2\text{OH}^- \rightarrow \text{AgO} + \text{H}_2\text{O} + 2e$ [OH ⁻] falls during charge. [HOH] rises during charge.	On zinc plates: $\text{ZnO} + \text{H}_2\text{O} + 2e \rightarrow \text{Zn} + 2\text{OH}^-$ [OH ⁻] rises during charge. [HOH] falls during charge.	Membrane present. Water transferred out. <i>Electrolyte level falls.</i>	Membrane present. Water transferred in. <i>Electrolyte level rises.</i>

^a All processes shown are reversed during discharge.

^b Cd(OH)₂ is a preferred reactant. Reaction written to show consumption of H₂O.

may be a factor in the transfer of solute through the separator. The study is continuing and more information is becoming available each month. The use of pillows and bellows and other mechanical devices for level control may be established as a rather inefficient method of achieving the desired end in view of the limited space available in the battery and in view of the inherent limitations of all such mechanical devices. Yet this investigation, or one which should follow it, may lead to the specification of separators which will possess the optimum transfer properties for any cycle of charge and discharge required for the end use.

Similar chemical modifications of membranes to control electro-osmotic flow have

been achieved in liquid separation processes by a formulation of the membrane to control the type and density of the fixed ionic charge. The solute flow is affected also by the degree of membrane swelling, another characteristic controllable by membrane formulation. A similar control of electro-osmotic flow has been achieved in fuel cells using ion-exchange membrane electrolytes.

The separators employed in the cells which were the subject of the Goddard work were of cellulose. Such cells are subject to the electro-osmotic flow from the positive to the negative compartment on charge and in the reverse direction on discharge. Cellulose assumes a negative charge in alkaline media owing to a moderate carboxyl content of the

polymer. The electrolyte absorbed within the separator assumes a corresponding positive countercharge, which is responsible for an electro-osmotic flow in the direction of an imposed negative potential.

Although this effect is significant for cellulose separators, it is of much greater importance for radiation-grafted polymer membranes. This has resulted in certain seeming anomalies. As an example of this, Lander and Keralla (ref. 12) found that in cycle life tests of 25 AH cells, failure by washing of the zinc-active material was more pronounced, the greater the number of layers of the separator, a polyacrylic acid grafted polyethylene. The authors state: "The reason why the cells with 6 and 8 layers failed earlier was due to earlier washing of the negative plate active material, but why this happened is not obvious." In other studies (refs. 13-16) it is shown that the failure and loss of capacity by negative-plate washing is dependent on the quantity of electrolyte in the cell and also greatly dependent on the depth of discharge. Thus radiation-grafted separators tend to compare favorably with cellulose when comparison is made at shallow discharge levels, but the opposite may be true at greater discharge depth.

TABLE III—*Acrylic Acid-Grafted Polyethylene Cycles to Failure*

[From Lander and Keralla (ref. 12)]

Cell No.	Four layers	Six layers	Eight layers	Fibrous sausage casing
1 ----	1368	984	804	1236
2 ----	2350	996	984	1788
3 ----	2362	984	828	1356
4 ----	2446	1116	576	-----
5 ----	2674	840	984	-----
6 ----	(a)	1188	792	-----
7 ----	(a)	828	396	-----
8 ----	(a)	840	528	-----
9 ----	(a)	1116	444	-----
Mean ---	2458+	988	704	1460

^a Still cycling when data collected.

One example of this effect (from Lander and Keralla) is seen in table III. The results are all explicable on the basis of a depletion of the positive-plate electrolyte during the charging cycle, causing a concentration of the current at the lower part of the negative plates. During discharge the negative-plate electrolyte level is higher. This tends to corrode the zinc plate at the upper part without a corresponding restoration on charging.

A fairly exhaustive discussion of osmotic transfer of solvent and electro-osmotic flow is given by Tuwiner (ref. 17), in terms of membrane segmental diffusion (pp. 158-161, ref. 17), phenomenology (p. 168), and membrane (pp. 178-179). Structural factors in electro dialysis and in the blistering of polymeric coatings are also treated (pp. 25-30 and p. 243).

ZINC DENDRITE PENETRATION OF MEMBRANES

Power-source development efforts at Goddard Space Flight Center also have been directed at determination of the mechanism of zinc dendrite formation and the mechanism by which the zinc dendrites penetrate a separator. Two programs, reported by Oswin (ref. 18) and Stachurski, Dalin, and Solomon (ref. 19), are interrelated.

The first program was limited to a study of the morphology of zinc crystal dendrite formation. It was shown that there is a definite progression from mossy to acicular, together with intermediate modifications, as the potential of the zinc plate is made increasingly cathodic. The study appears to indicate that the dendrite form is affected by the electrode potential rather than by the concentration of zincate or potassium hydroxide in the electrolyte. Photographs indicate typical dendrite structure, but are too blurred and indistinct to reveal the crystal in a definitive manner.

The second program was for the purpose of determining the mechanism by which the zinc is deposited within a separator in the charging of a battery and the manner in which the zinc dendrites penetrate. The

first part of the study was concerned with the morphology and electrochemical kinetics for zinc crystal growth within the electrolyte and within the separator.

To study the growth process, a microcell was designed to cause the formation of various types of zinc crystal growth or of membrane penetration within the field of view of a microscope which provided a magnification of $100\times$ at the photographic image plane. Instrumentation covered the development of zinc crystals cathodically from 30 percent potassium hydroxide saturated with zinc oxide.

The photomicrographs indicate the morphological types under potentiostatic control of polarization and overvoltage potentials affecting growth rate. They are of practical value, since one may be able to glean some information from them concerning the operating conditions in a working battery after tearing down a cell for examination.

The conclusions with regard to dendrite penetration of the membrane are of ques-

tionable applicability, inasmuch as the investigators note that the cellophane membranes were never penetrated when the cell was operated under potentiostatic control. They then went to a galvanostatic method of operation using a constant current of 1 milliamperes (5–10 ma/sq cm). Gradually the space between the separator and the cathode becomes filled with a zinc foam, after which conical crystals penetrate the separator. It may be surmised, however, that the current density is here extremely high, inasmuch as the foam at the interface between the separator and the solution acts as a current insulator.

The pictures at $100\times$ are blurred and indistinct, revealing little of the morphology of dendrite penetration. This is true of the penetration of the separator by galvanostatic operation, as well as of the pictures of representative penetration of a modified cellophane separator in a working silver-zinc cell. This work may be the forerunner of other investigations, however, which may reveal the true mechanism of membrane penetration by zinc dendrites.

CHAPTER 5

Fuel Cells

The goal of NASA's fuel-cell program is to obtain lightweight, dependable power sources for a variety of needs. (See figs. 10-12.) These include communication, command and control, guidance, radar, image acquisition, processing and transmission, data handling and storage, life support, experiments on planetary surfaces and environment, and power for surface exploration vehicles.

Power requirements have continued to increase as missions have grown longer. On short missions it is feasible to carry water, but at some point life-support systems for water recovery from body wastes become necessary. These systems involve a substantial requirement of energy.

The carbon dioxide of the atmosphere may

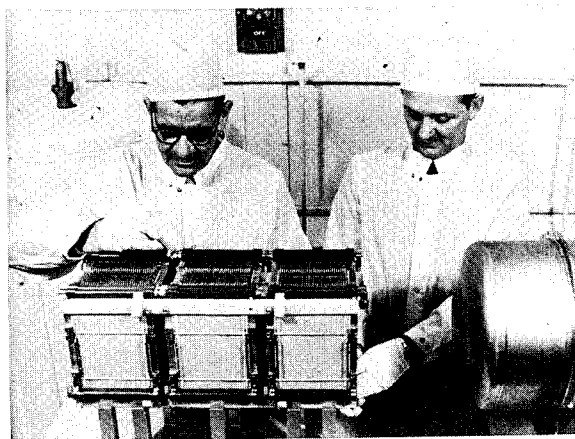


FIGURE 10.—Interior and canister of Gemini fuel cell [From: E. M. Cohn, "NASA's Fuel Cell Program" in "Fuel Cell Systems," p. 2. *Advances in Chemistry Series 47*, American Chemical Society.]

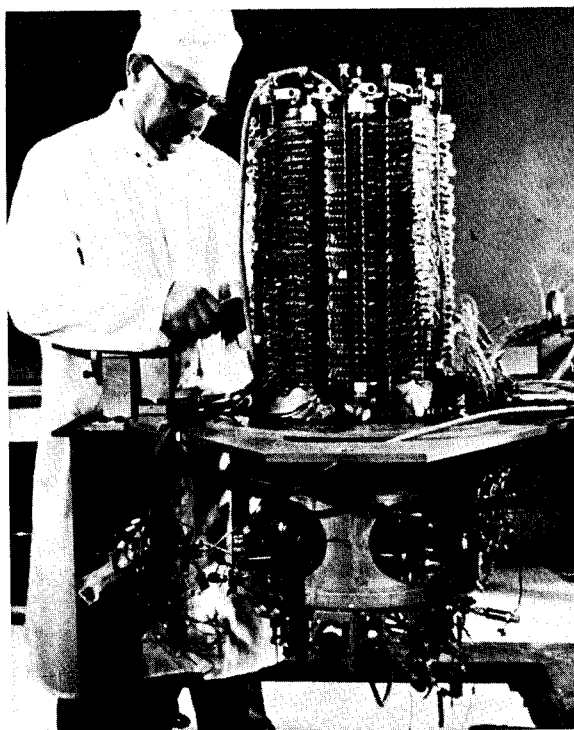


FIGURE 11.—Module of Apollo fuel cell. [From: E. M. Cohn, "NASA's Fuel Cell Program" in "Fuel Cell Systems," p. 3. *Advances in Chemistry Series 47*, American Chemical Society.]

be dealt with by chemical absorbents on short missions. However, it becomes essential to employ a cyclic process of absorption and desorption or multiple-stage permeation separation after a certain point.

Hydrogen-oxygen fuel cells produce water and attempts have been made to render this water potable. Alternately, the water may be electrolyzed with an expenditure of energy to regenerate hydrogen and oxygen.

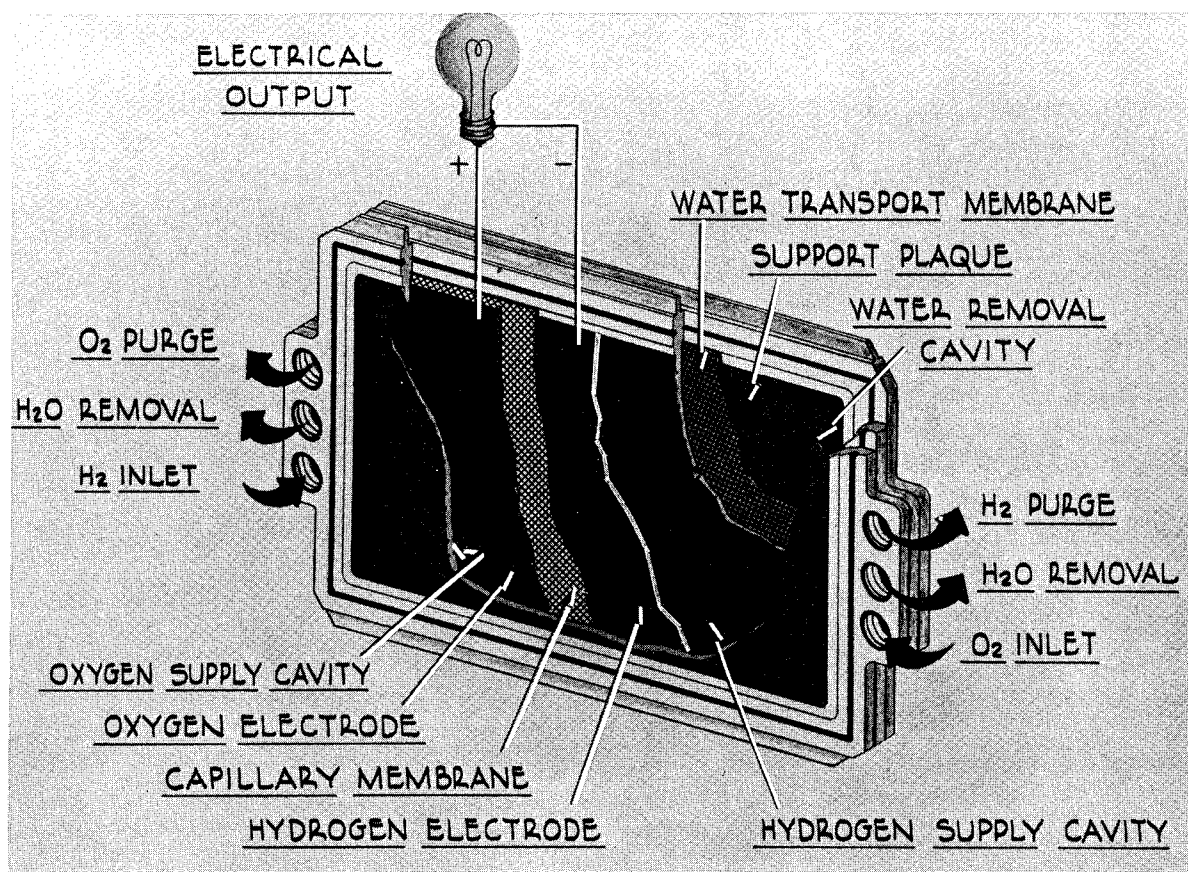


FIGURE 12.—Schematic diagram of fuel cell with passive water removal system. [From: E. M. Cohn, "NASA's Fuel Cell Program" in "Fuel Cell Systems," p. 5. Advances in Chemistry Series 47, American Chemical Society.]

The energy may be obtained in this case with solar cells. The system then becomes equivalent to a secondary battery but with greatly reduced weight requirements.

Two types of fuel cells which involve the use of ion-exchange membranes are currently being developed by NASA. Both types of membrane fuel cells are competitive with various other types of fuel cells requiring no membranes. The cells depend on porous or permeable electrodes or upon a solid electrolyte (a kind of membrane) capable of conducting oxygen ions. A modified Bacon fuel cell (which requires no membrane) has been selected for the Apollo vehicle and its Lunar Excursion Module.

Each type has merits and limitations and no one type is likely to supersede the others

for all applications. It is necessary to consider such factors as type of fuel, weight and size limitations, temperature and coolants, product utilization or disposal, and continuous or intermittent operation.

Fuel cells are also, to a degree, competitive with both primary and secondary batteries. This has become more widespread with the reduction of weight in the last 2 years to about 70 to 100 pounds per kilowatt, exclusive of fuel and fuel storage.

With regard to potential competition with secondary batteries, there is an effort underway on a secondary, or regenerative, fuel cell: a low-temperature hydrogen-oxygen cell with electrolytic decomposition of water. This is quite attractive on the basis of the high-energy-storage equivalent of hydrogen

and oxygen per unit of weight, especially when the hydrogen-oxygen generation and the fuel cell are combined in a single unit as described in reports by Electro-Optical Systems, Inc., under NASA Contract NAS 3-2781.

SINGLE-MEMBRANE FUEL CELLS

The membrane fuel cell developed by the General Electric Co. is based upon a single-membrane layer which constitutes the electrolyte. The membrane layer separates the electrodes which are applied to either side in the form of a platinized carbon layer backed by a current-collecting metallic screen. The electrodes are within the gas spaces of the cells, hydrogen on one side, and oxygen on the other. The hydrogen gas dissolves in the electrode and passes into and through the membrane electrolyte as hydrogen ions to the oxygen electrode. The ions react to deliver a positive charge and form water which is collected from the oxygen cells.

This type of fuel cell has the great merit of efficiency, simplicity, and compactness. Its greatest disadvantage is that a single pinhole may constitute a passage within which oxygen and hydrogen can react violently in the presence of the platinum catalyst and soon destroy a large part of the membrane—rendering the entire fuel cell inoperative.

Although the problems of obtaining satisfactory reliability in single-layer membrane fuel cells are formidable, they have been satisfactorily resolved in NASA's program to obtain lightweight, dependable power sources, and such cells are used in the Gemini spacecraft. As in other programs of this kind, there was no absolute assurance of success until the completion of the massive efforts to produce the final hardware.

Although the single-layer membrane fuel cell has advantages in terms of power output per unit of weight and size, its applicability to industrial and consumer uses remains in some question. Its inherent vulnerability to pinhole defects is such that achievement of reliability may be costly in terms of mem-

brane manufacture and inspection labor. There are problems, too, of membrane-aging effects which affect the transfer properties and gas permeability.

DUAL-MEMBRANE FUEL CELLS

Another type of membrane fuel cell, without inherent vulnerability to pinhole defects, is one in which a liquid electrolyte is placed between two membranes. On the gas side of each membrane a hydrogen and oxygen electrode is applied. It is similar in structure to that of the single-membrane fuel cell above. Although this type of fuel cell is not extremely vulnerable to pinhole porosity, it has the disadvantage that the water which is formed by the union of hydrogen and oxygen is not easily removed because it is produced within the liquid electrolyte which thereby becomes diluted.

As a solution to the problem of electrolyte diffusion in this type of fuel cell, a so-called "osmotic still" has been developed (ref. 20). To concentrate the acid electrolyte of the dual-membrane fuel cell and to recover this water, the water to be removed from the electrolyte was diffused through an ion-exchange membrane into a partially evacuated vapor space from which it was removed by condenser cooling. Actually, this system offers no advantages over a simple distillation, except that it appears to permit separation of liquid and gas phases under conditions of zero gravity.

Inasmuch as a liquid-vapor interface is not readily maintained in the absence of a gravitational field or under zero-G space conditions, a membrane serves to maintain an interface between the liquid and gaseous phases.

The electrolyte is a 6 *N* solution of sulfuric acid. One pound of water is produced from hydrogen and oxygen for each kilowatt-hour, approximately 48 pounds per day, for a nominal 2-kilowatt fuel cell operated at its maximum capacity. External heat is not required, as the operation of the fuel cell results in heat generation within the electro-

lyte owing to electric current flow and internal resistance.

Some interesting test results are reported by Walsh and Leovic (ref. 21) for the full-scale prototype unit of 2-kilowatt capacity. This contained 7 square feet of membrane supported in a stack arrangement by Trilox and Monel screen coated with Kel-F. (See figs. 13 and 14.) Alternate cells for the acid solution and the vapor are provided by the stack. The acid enters at about 200° F and leaves at about 192° F, producing vapor at about 5 psia. The water obtained by condensing this vapor has a pH about 5.0. Various membranes were evaluated in this study and an AMF ion-exchange membrane was found to be best.

CONSTRUCTION OF SINGLE-MEMBRANE CELLS

The problems in the construction of single-membrane fuel cells are extremely complex and require for their solution a very high order of technical competence. They are associated first with membrane formulation and production; next with the electrode composition and configuration; and, finally, the stack assembly.

The membranes must be subjected to extremely close and careful quality control and inspection to eliminate pinholes—which cannot be tolerated. They must have the requi-

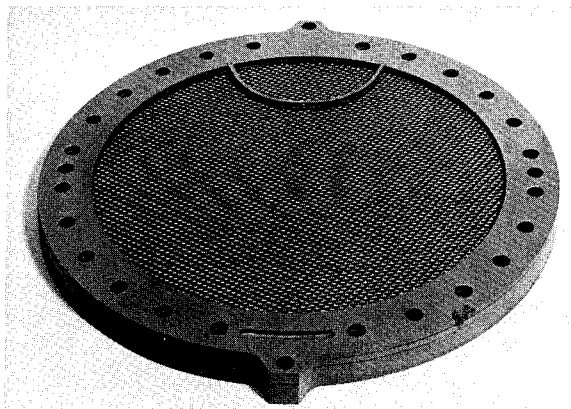


FIGURE 13.—Electrolyte cavity for 2-kilowatt osmotic still. Tulox mesh and membrane removed to show Kel-F-coated Monel support screen. [From: Walsh, T. J. and Leovic, W. J., Chem. Eng. Prog., vol. 61, 80 (1965).]

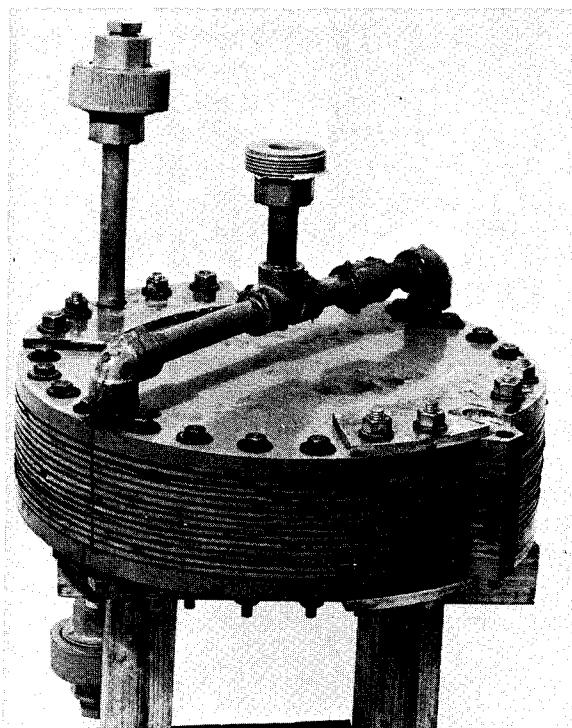


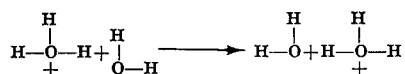
FIGURE 14.—Assembled 2-kilowatt osmotic still showing an inlet line (top left) and water vapor outlet line (top right, bridged). [From: Walsh, T. J. and Leovic, W. J., Chem. Eng. Prog., vol. 61, 81 (1965).]

site electrical conductivity, yet must permit a minimum of hydrogen diffusion which leads to a reduction of the current efficiency. In the operation of the fuel cells, there appears to be a tendency to leach some of the lower molecular weight polymer from the membranes, thus resulting in a progressively higher diffusion of the hydrogen.

Standardized procedures have been set up to measure this effect and to establish production and quality-control methods to minimize the diffusion of hydrogen initially and after a prescribed period of specified service. Polymerization must be controlled to yield membranes with a high molecular weight and moderate molecular-size distribution range and with a considerable amount of crosslinkage without undue sacrifice of mechanical toughness and conductivity.

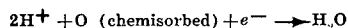
The electrodes are made by cementing platinized carbon upon a face of each mem-

brane. The electrode is backed with a woven wire screen called a collector, which distributes or collects the current from the carbon granules. The hydrogen electrode is one face of each membrane; the oxygen electrode is the other. When the gases are admitted, each to its appropriate side, hydrogen gas dissolves into the platinum. Electrons are transferred to the granules and from these to the collector wires and the outer circuit. At the same time the protons which remain are transmitted to the water which may be considered to be dissolved in the membrane. Here it becomes hydronium, which is subject to a proton transfer to neighboring water, indicated by Tuwiner (ref. 17) as follows:



The proton skips in the manner indicated from one water molecule to another until it reaches the opposite face where it encounters the platinized granules which are a part of the oxygen electrode.

Here it is absorbed again as protons. These react with the oxygen which is chemisorbed by the platinum surface. A surface reaction on the platinum results in formation of water while electrons are drawn from the collector wires and the outer circuit.



The water is collected as a liquid which drains from the oxygen electrode surfaces. Under conditions of zero G, this would flow out with the oxygen off gas.

The stack assembly must be designed and

constructed with considerable care to avoid an internal gas leak which would cause an immediate burnout. Fuel and oxygen must be delivered and distributed throughout. Heat must be removed, and also the water which would otherwise cause a "drowning" of the fuel cell with consequent loss of capacity.

The single-membrane fuel cell is one of the most compact power sources that can be devised. The electrolyte is the membrane itself, about 30 mils in thickness, and the product water is delivered free of contamination. Conversion efficiency may be very high.

Against these advantages there is the fact that this type of fuel cell is, for reasons that are obvious from the previous discussion, very expensive to build. Although there is, at this writing, no clear and obvious method of reducing the cost to an extent that would appear to open the door to commercial utilization, some way may be found to make this a possibility.

One very important step toward solution of the problem is to obtain a bond between a membrane which imbibes water and an electronic conductor. This bond, to be sound and serviceable, must resist or avoid differential expansion due to humidity and thermal effects. Probably there should be an intermediate layer in which the water-imbibing polymer and the electronic conductor are interdisseminated within a network. For the oxygen electrode, the network must provide access for the gas.

CHAPTER 6

Separation Processes

Separation processes fall into two main categories; viz, those pertaining to gas-permeation and those pertaining to liquid-permeation processes.

GAS-PERMEATION PROCESSES

Gas-permeation processes depend upon pressure as a driving force to achieve an enrichment of a gas stream with respect to one or more components in a mixture. NASA studies in this area have been for the purpose of developing life-support systems in which carbon dioxide may be removed from an airstream to maintain the concentration at a reasonable level for life support while removing in concentrated form the carbon dioxide which is produced by respiration or combustion.

For many years the recovery of helium from natural gas by membrane-permeation methods has been proposed and studied. It has been concluded, subject to further advances in the art, that the permeation process is not economically competitive with refrigeration as a method of recovering helium. Advances in gas permeation, as developed by NASA and by the Air Force in life-support systems, however, may alter the situation.

The membranes that are best for helium are not the same as those preferred for carbon dioxide separation, and the scale of operation in life-support systems is far smaller than that required for the industrial process. Nevertheless, the principles of permeation, methods of membrane formulation and evaluation, and the techniques of ob-

taining the most compact, practical system for supporting the membranes in an assembly in which the permeation process may be conducted, are to a degree comparable in the two processes.

In evaluating the likelihood of commercial adaptation of the processes and equipment which NASA has developed as parts of life-support systems for carbon dioxide removal, cognizance must be taken of certain inherent limitations with regard to energy requirements. Gas permeation is an irreversible process in which a considerable amount of energy of compression is irretrievably lost when the gas mixture permeates the membrane. This is most serious where the gas is to be recovered from a relatively low level of concentration, as in the case of carbon dioxide from the atmosphere or helium from natural gas. The energy of compression in the feed gas which does not permeate the membrane may be recovered as mechanical energy only in part by its expansion. This limitation is of greatest concern in systems of gas recovery from low concentration.

When the desired component is present in larger concentration, and when the membranes have a high degree of selectivity, good energy efficiency is possible. At present, certain metallic membranes are known to possess excellent selectivity. Palladium alloys are capable of serving as a highly effective means of recovery of relatively pure hydrogen, and silver alloys are an effective means for the separation and recovery of oxygen. NASA-sponsored research has led to the development of membranes providing

excellent mass-transfer properties with unprecedented resistance to chemical attack, oxidation, and high temperature.

In gas-phase-separation processes there are potential applications which await development. NASA-developed technology has aided development of silicone-based membranes which are selectively permeable to carbon dioxide and other membranes which are usable in helium and hydrocarbon separations. There is already consideration of using silicone membranes in a device to permit divers to utilize oxygen dissolved in sea water in a transfer process in which the oxygen is exchanged for the carbon dioxide that is exhaled.

LIQUID-PERMEATION PROCESSES

Among liquid-permeation processes which are, or might be, conducted on a large scale industrially, we may include dialysis, electro-dialysis, and reverse osmosis (or ultrafiltration).

In each case industrial development depends upon the development of new and improved membranes. Part of this improvement may be directed toward improved capacity and/or specificity. Other significant improvements may be made in the physical and mechanical aspects of membrane technology. In the latter category we may consider improvements directed to obtaining very thin membranes which are reasonably free of hole porosity or localized mechanical defects that might impair the usefulness of such membranes in large-scale separation processes. Mechanical strength, resilience, and toughness are also factors in performance.

WATER RECLAMATION FROM URINE BY REVERSE OSMOSIS

Attempts have been made to separate water from urine by membrane processes, including electro-dialysis and reverse osmosis. Although no insurmountable difficulty with the removal of salt is encountered in either method, urea and other nitrogenous components do not respond to either method of

treatment without some type of pretreatment.

Among the methods which have been considered or tried experimentally are: the formation of an insoluble adduct of urea, conversion of ammonium carbonate by urease-catalyzed hydrolysis, absorption using activated charcoal, chemical oxidation using calcium hypochlorite, and electrochemical oxidation.

With regard to the first of these, there is no adduct known which will yield a product with urea which is sufficiently insoluble without excessive penalties. Ammonium carbonate is not sufficiently ionized to permit its removal by electro-dialysis while the ammonia is not sufficiently rejected in reverse osmosis. Addition of an acid permits rejection of the ammonia in either method, but this is considered impractical because it merely adds to the penalty of treatment in terms of weight and energy.

The same practical considerations weigh against the use of calcium hypochlorite or other oxidizing chemicals. Electrolytic oxidation, on the other hand, requires only a small cell for the oxidation, a phase separator for removing the gaseous products, carbon dioxide, nitrogen, and hydrogen. The energy required for electrolysis is 457 watt-hours per liter. This is based on a cell voltage of 3.8 to 5.4 volts and a current efficiency of approximately 65 percent.

After the electrolytic treatment is completed, the urine is nearly free of organic nitrogen by Kjeldahl analysis and contains only small amounts of the more refractive chloramines and traces of chlorinated hydrocarbons, all of which are readily removed with activated charcoal. Several parts per million of residual active chlorine assure the complete sterility of the solutions.

As a part of a study to determine the effect of all the significant variables on the rate of water permeation and on the salt concentration, Everett and Scardaville (ref. 22) performed one of the most comprehensive studies of the effect of the elapsed time, measured from the initial application of pressure, upon

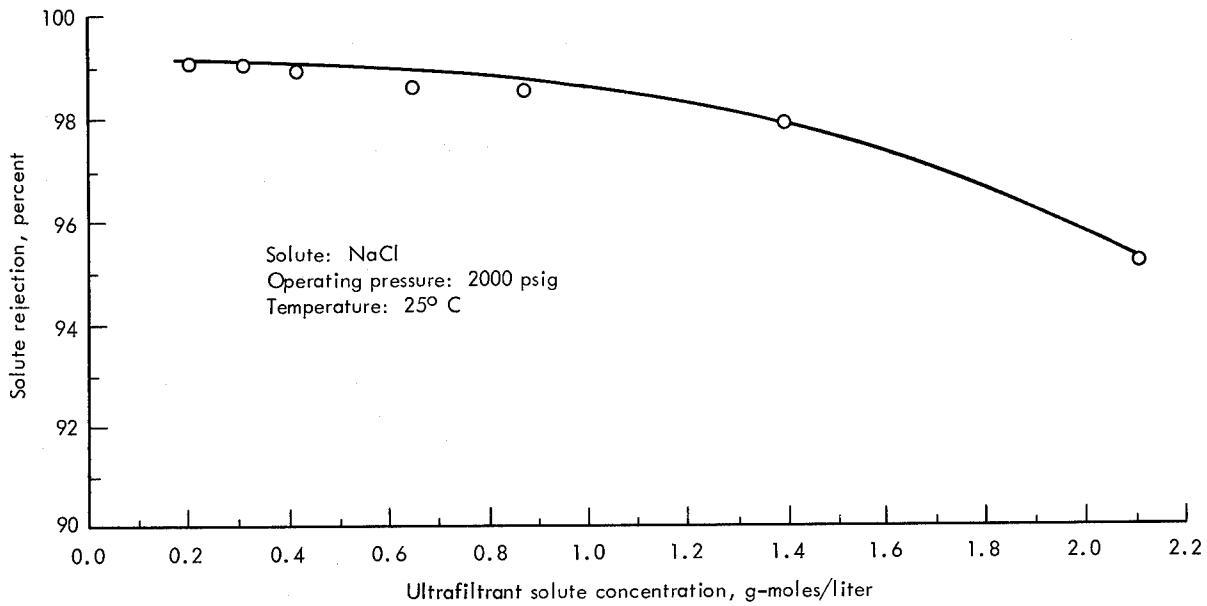


FIGURE 15.—Membrane solute rejection capability as a function of ultrafiltrant solute concentration.

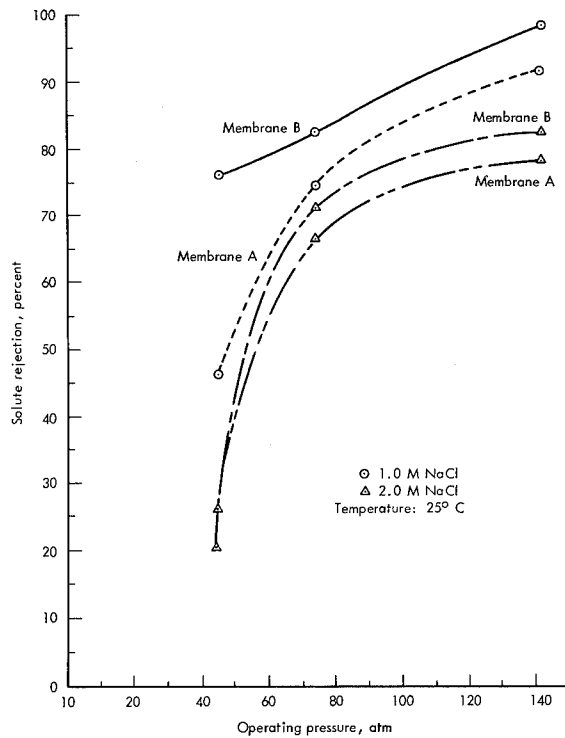


FIGURE 16.—Membrane solute rejection capability as a function of operating pressure plotted parametrically with respect to ultrafiltrant solute concentration.

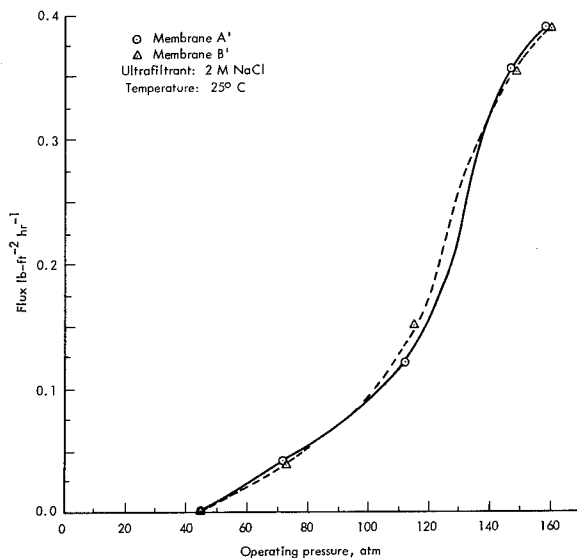


FIGURE 17.—Flux transmission as a function of operating pressure for 2.0 M NaCl ultrafiltrant.

the permeation flux and the salt concentration of the ultrafiltrate using a 2.0 M sodium chloride feed.

Approximately 50 hours were required for a steady state to be established. During this time there appeared to be a compaction of the membrane. The decrease in the flux amounted to approximately 50 percent in most cases. Other variables studied included the operating pressure and the salt concentration.

Results are shown in figures 15, 16, and 17. The effect of pressure was to increase the flux but, because of the compaction due to the pressure, the flux increase was not proportional to the increase of pressure.

Both the flux and salt rejection are adversely affected by increase in the feed concentration. This is best shown by relating the flux and the ultrafiltrate concentration with the ultrafiltrant salt concentration. Unfortunately, the membranes developed by Everett and Scardaville (ref. 22) do not possess the same capacity, expressed as water flux, as the best membranes developed by Loeb and coworkers. Furthermore, reproducibility of the membrane properties was not good.

In the latter part of a contract study (ref. 23), the film casting method of Manjikian (ref. 24) was employed using a solution consisting of 25 percent cellulose acetate, 30 percent formamide, and 45 percent acetone in place of the solution of Loeb and Souririjan (ref. 25), which consists of cellulose acetate, acetone, water, magnesium chloride, and hydrochloric acid. The results employing the former solution were much more readily reproduced and the capacity of the films in terms of product water volume were very nearly the same (about 19 gallons per square foot in 24 hours for a pressure of 1500 psi).

In commercial applications of membrane technique, the design and construction of the equipment for supporting the membranes are as important to the technical and commercial success of the process as the membrane composition and properties. In the desalination of sea water by reverse osmosis, the membrane capacity under the most favorable conditions is about 10 to 15 gallons daily for each square foot of membrane surface. The cost of the membrane itself may be reduced to well under a dollar per square foot and the service life may, hopefully, be extended reasonably. However, the capital cost of the equipment to support enough of the membrane to provide a capacity of multimillion gallons per day, using a pressure of about 2000 psig, is likely to be very substantial.

A project supported by NASA's Langley Research Center has led to a new design concept of a unit for reverse osmosis in which the membranes are arranged in pairs in a stack, each pair composed of circular membrane sheets separated by a woven wire cloth and nylon paper; a single hole through the five-layer sandwich near the periphery permits the flow of the feed solution from cell to cell along the stack. The solution becomes more concentrated in each successive cell until it attains the concentration of the brine at the discharge. The cylindrical assembly has circular end plates of 1/2-inch-thick titanium with holes for tie bolts about

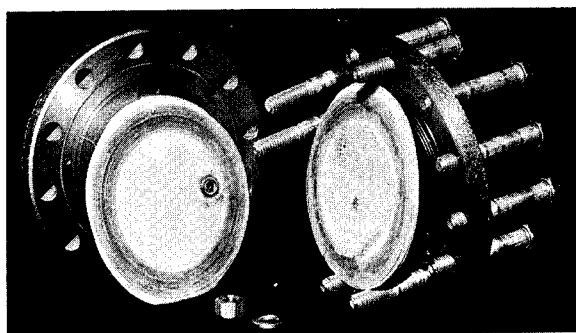


FIGURE 18.—Reverse-osmosis assembly, open. Titanium end flanges and two subassemblies. It is possible to use an indefinite number of these depending on the capacity that is required.

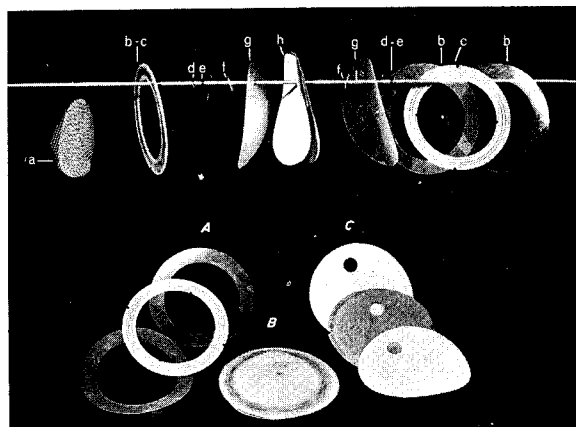


FIGURE 19.—Reverse-osmosis subassembly. *a*. Double layer of polyethylene screen. *b-c*. Spacer ring and two polyethylene gaskets at left-hand end of supporting rod and at *B* below. Expanded components shown at right-hand end of supporting rod. *d*. The female grommet. *e*. Quad ring. *d-e*. At the right, the quad ring is on the cylindrical section of the male grommet component. *f*. Polyethylene gaskets, which are cemented around the holes in membranes *g*. *h*. Nylon paper layers and layer of woven and centered wire screen (expanded view in *C*). *A*. The complete subassembly.

the circumference. Bolts are used to hold the stack assembly together and maintain a tight system under the required pressure of 1500 psig. Each end plate has a connecting fitting for pressure tubing which delivers the feed stream at one end, and carries away the concentrated brine at the other.

The construction of the end plates and other parts is shown in figure 18. Figure 19

shows the construction of a spacer. The latter consists of a flat ring constructed of epoxy-resin-impregnated glass-fiber cloth. The thickness of the ring is 0.0254 inch. The outer diameter is 4 inches and the inside diameter is 3 inches.

Bonded to the flat faces of the ring are a series of concentric flat copper rings 0.0048 inch in thickness. There are three of these rings on one side of the epoxy ring and two on the other. The width and spacing of these copper rings or ridges is such that when two spacers are brought together face to face, the opposing copper ridges interlock with a clearance of 0.056 inch.

In each membrane pair subassembly there are placed between the enveloping spacer rings two polyethylene gaskets of 0.012 inch thick, two layers of membrane 0.005 inch thick, two nylon paper layers 0.01 inch thick, and a single layer of woven wire cloth 0.0036 inch thick. This combined multilayer assembly is 0.038 inch thick, not including the thickness of the spacer rings. With a clearance between interlocking copper ridges of 0.056 inch, there is a considerable pinching of the layers within the clearance between concentric copper ridges. This has the effect of imparting a self-centering property and also of holding a seal between the separator rings and the membranes which is watertight under 1500 pounds psi pressure.

The copper ridges are fabricated by employing the technique developed for printed circuits. The starting material is a laminate consisting of epoxy-resin-impregnated glass cloth with copper foil bonded to both faces. The exposed surfaces of the copper are coated with a photo resist which is exposed to light from a master transparency. Unexposed portions are washed away and the copper removed by etching in a solution of ammonium persulfate. Where the photo resist has been exposed and hardened, the copper remains as an etched pattern.

Because of the methods used, the pattern of concentric circular ridges is reproduced very precisely and the method is capable of

producing any number of perfectly interchangeable parts. The ultimate tensile strength of the plastic composition is 40 000 to 60 000 psi and the copper is bonded to conform with rigid peel-strength specifications.

Concentricity of the spacer rings and the copper ridges is insured by the self-centering property. This results in a uniform peripheral distribution of the pressure on each spacer, provided that the tie bolts are tightened uniformly.

The assembly of the reverse-osmosis apparatus involves the prefabrication of membrane pair subassemblies. (See A in fig. 19.) Each of these subassemblies consists of two parallel and concentric 4-inch-diameter membranes separated by, and supported on, a base consisting of a woven wire screen and two layers of nylon paper. The subassembly is designed so that the pressure upon the outer faces of the membranes may be as high as 1500 psig, while the hydrostatic pressure at the inside faces of the membranes is nearly zero. The differential pressure of 1500 psi compresses each membrane upon the supporting base. The water diffuses through each membrane, flows into the supporting base, and then flows laterally toward the periphery of the supporting base and out of the stack.

Construction of the membrane pair subassembly is completed with two spacer rings, one against each of the outside faces of the two membranes. The spacer rings are concentric with the membranes and their base support, and there are two polyethylene gaskets, 0.003 inch thick, one between each membrane and its opposing spacer ring. In the subassembly the side of a spacer ring having three copper ridges opposes a two-ridge side of the other spacer.

The supporting base for the two membranes of the subassembly is composed of a layer of woven and sintered stainless-steel screening and, on either side of the screening, a layer of nylon paper. The selection of the screening (Rigimesh K) and

nylon paper was made after extensive testing and evaluation of alternatives.

When the membrane pair subassembly is placed in compression in the stack assembly, the layers between the spacer rings are molded into a W-shaped configuration. This imposes a severe strain on each layer owing to the stretch in the lateral, and the compression in the transverse direction. The plastic membranes and gaskets and the fibrous nylon conform readily. The screening, however, is subject to considerable tensile stress radially. Despite this stress, which exceeds the yield point, the screen structure does not collapse or break and the water which is transferred by reverse osmosis flows laterally, not merely within the 3-inch-diameter space inside of the spacer rings, but also along the part subjected to stress as a result of compression of the membrane stack.

To satisfy the requirement for communication between the cells containing pressurized mineral-containing solution, it is necessary to provide an opening through both membranes and the supporting base of each membrane pair subassembly. This opening permits communication between the two sides of the subassembly, but it must avoid communication with the low-pressure pure water in the space between the membranes. There must be no significant leak of the pressurized brine into the permeate water through the peripheral seal between each membrane and its contacting spacer or through the wall of the hole through the membrane pair subassembly.

To fabricate the pressure-tight hole through the membrane pair subassembly, the following concentric hole sizes are cut in the component layers, the center of each hole three-fourths inch from the outside edge:

Woven and sintered screen: $\frac{5}{8}$ -inch diameter

Nylon paper layers (2): $\frac{9}{16}$ -inch diameter

The woven screen, with a layer of Viskon nylon paper on each side, and with the holes aligned concentrically, is assembled with two 0.012-inch-thick polyethylene flat gaskets, each $\frac{13}{16}$ inch in diameter with a $\frac{1}{8}$ -inch center hole. The gaskets are placed on each outside face of the nylon paper disks and they are positioned to be concentric with the holes in the nylon paper and the screening. By means of an adhesive the gaskets are bonded to one another on the inside and to the nylon layers around the peripheries of the gaskets. Adhesive is next applied to the outer faces of the gaskets and to the opposing surface of the two membrane disks which are mounted on either side of the screen and nylon paper assembly. Finally, $\frac{9}{16}$ -inch gaskets with $\frac{1}{8}$ -inch holes are bonded to the outsides of the membranes after being positioned to be concentric with all the holes. The adhesive is permitted to cure while the components, immersed in water, are held together under pressure. The $\frac{1}{8}$ -inch holes are then punched through the membranes and sealed with No. 00 G&W grommets.

The membrane pair subassemblies are then assembled in the stack. Figure 18 shows two of these subassemblies placed between the end plates. The assembled stack may contain any number of membrane pairs. One end plate contains the inlet hole for the solution feed. When the first membrane pair is inserted, it is placed so that the position of its grommet hole is diametrically opposite the inlet hole of the end plate. The other membrane pair subassemblies are then placed with the grommet holes alternating diametrically. Finally, the exit hole which is in the second end plate is located diametrically opposite the position of the grommet hole in the last membrane pair subassembly. This provides for an alternating flow of the feed solution as it traverses the membranes.

Two layers of eight-mesh polyethylene screen are employed to fill some of the space of the pressurized cells within the inside diameter of the spacer rings. This serves the purpose of restricting the movement of the subassemblies and also of preventing the lip

of any grommet from touching the face of an opposing membrane and thus restricting or closing off the flow of the solution from cell to cell along the stack. This technique permits the construction of extremely compact stack assemblies, inasmuch as the frames may be made very thin, permitting as many as 25 membranes to the linear inch of stack thickness. Such construction is applicable to gas permeation units as in the separation of helium from natural gas in which a stream of compressed gas is carried over a membrane.

DIALYSIS

Improvement is needed in the capacity of membranes now used in large-scale dialysis. This is difficult to achieve because vinyl-base materials now available are extremely permeable and quite resistant chemically. Considerable improvement in capacity could result from a reduction in membrane thickness. The present standard is 4.5 mils. If this thickness could be reduced one-half, the capacity of each dialysis unit now being used could be doubled and the capital investment halved accordingly. Certain techniques for very thin membranes developed by NASA should be applicable, and if these techniques were exploited it is probable that a great expansion in the applicability of dialysis would result.

Potentially very large-scale applications, e.g., recovery of spent sulfate pickle liquor from the steel industry, might become economically feasible. Present limitations are imposed by the considerable capital investment required for the recovery of sulfuric acid having little value per ton. The volume of spent acid wasted by the steel industry is very large, and improved membrane methods could alleviate the problem of waste disposal.

In addition to the limitation in capacity of membrane materials for dialysis, there is a temperature limitation which the thermoplastic materials now used will withstand. They are not recommended for continuous service above 120° F. Techniques developed in the course of NASA studies

have indicated possibilities of crosslinkage to improve greatly the resistance of these materials to elevated temperatures.

At this writing, Ames Research Center is contemplating research efforts to develop a method of carbon dioxide separation in a life-support system which would be feasible from the standpoint of equipment size, and weight and energy requirements. The system would have to incorporate a very large membrane area in a compact, light unit. The membranes must be thin, and highly permeable, with a selectivity ratio of carbon dioxide to air of at least 6:1. Also, a means is needed for recovering the energy of compression of the nonpermeating fraction of the gas stream which enters the unit. Since only about 20 percent of the gas permeates the membrane in each stage, the efficient recovery of this compression is vital to the successful application of the process.

The mechanical design for a compact arrangement of the membranes and the use of

thin and highly permeable materials provides a very efficient unit from the standpoint of compactness and weight. A membrane which is highly selective with regard to carbon dioxide is necessary to minimize the number of stages and also to contribute to reasonably good energy efficiency. This is the case because the permeation of the membrane by oxygen and nitrogen corresponds with a loss of compression energy which is equivalent to that necessary to recompress the permeating gas.

The very stringent requirements of life-support systems in the NASA programs should be an effective stimulus to development of new and improved membrane materials as well as improved mechanical membrane supporting units and mechanical means for compression and energy recovery. There is no doubt that the objectives of this program can be achieved, and that this achievement will encourage industry to examine the possibility of changes in its gas-phase-separation methods.

CHAPTER 7

The Prospects Now

NASA efforts have contributed significantly to our Nation's technology in membrane production and utilization. Some of these efforts will aid in extensions of present programs. Thus silver-zinc batteries similar to those developed for spacecraft may be utilized in ground applications for communications equipment, guidance equipment, power tools, etc. Many future applications will result from assimilation of the technology and its extension to uses other than those for which this technology was developed. The same separators that are used in silver-zinc batteries for spacecraft, for example, are usable in nickel-zinc batteries on the ground.

To understand and appreciate the contributions of NASA technology, one must remember that until a comparatively few years ago no membranes comparable in permeability to ordinary cellophane were available on an industrial scale. There was literally no material which was usable in a practical sense as a membrane separator or dialysis membrane in mildly acid solutions or at even slightly elevated temperatures. Ion-exchange membranes had been developed, but their serviceability under moderately severe conditions was limited. There were no synthetic membranes less than 5 mils thick which were even moderately pinhole free.

Although many laboratory developments indicated the trends in membrane formulation and production, and numerous well-conceived theoretical studies of membrane behavior were available, commercial exploi-

tation was lacking. This was due in part to the heavy investment required and the uncertainties of commercial success. One company spent about \$250 000 for the development of membranes for electro dialysis and failed to sell even 1 square foot for this purpose.

Although a number of large-scale commercial dialyzers are now in service, the membrane requirements are moderate, inasmuch as the service life extends beyond 2 years. There is, consequently, little profit in producing membranes for sale. The same situation prevails with regard to membranes used as battery separators. Although the performance of the separators is vital to the successful performance of the battery, the profit to the membrane producer is relatively small. Developments in membrane production have tended to lag on this account. NASA requirements, however, have stimulated study of both production methods and facilities. Effects upon the civilian economy are already evident and there is now some commercial sale of membranes made by methods developed through NASA programs. Much more such stimulation is required to make this trend of real importance.

In an analogous development of membranes for desalination by electro dialysis, 10 years of programs supported by U.S. Government agencies were required before an electro dialysis industry was established. Once established, however, it continued to grow.

At present most of the producers of the

newer types of batteries derive much of their income from sales to NASA and the Department of Defense. Ultimately the sales of such batteries may be predominantly to the public.

Industrial firms that have participated in NASA contracts have ranged from large to small. The small firms appear to have been more strongly motivated to exploit the developments of contract research in products for the general market, while the large companies have tended to concentrate their efforts upon products which can be made and sold in great dollar volume. Only such membrane materials as cellophane seem to claim the attention of the larger producers. Similarly, only standard volume sales of primary and secondary batteries are of interest to the major companies. The specialties are left to the medium- and small-sized firms.

Much of NASA-developed technology consequently is of primary interest to small business which cannot afford the investment of large sums for research and development. Without this technology some of the vital new products, on which the growth of the national economy largely depends, may never see the light of day.

On the other hand, this technology is often directed toward the production of hardware whose cost is secondary to performance, weight, and power requirements. In application to civilian products, reevaluation is required, with greater emphasis on cost and

correspondingly less on other factors. Such reevaluation is possible only through careful study of the data available from the original sources and from the periodic progress reports.

In terms of economic importance, none of the areas appears more promising for future applications than that of power sources. Lead-acid batteries which account for the greatest dollar value require no membrane separators; nor do the Edison type and Nicad batteries. New and superior systems will require membrane separators, and the extent to which these newer types replace the older battery systems, or find new uses, depends in great measure upon the development of suitable membrane materials. Before the NASA-sponsored work there were literally no materials which could have been considered adequate for other than very limited application; viz, cellulosic materials in silver-zinc batteries. It is unlikely that the older types of primary batteries will be replaced by newly developed batteries employing membrane separators. There is, however, a possibility that for certain special uses a primary battery of a nearly infinite shelf life would be well received in certain consumer applications.

The future will undoubtedly bring standard utilization of liquid-separation methods involving membranes. In some industries these have already found acceptance and it is anticipated that their use will be increasingly widespread.

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