

ERDA/NASA/1002-77/2
NASA TM-73751

(NASA-TM-73751) ANION EXCHANGE MEMBRANES
FOR ELECTROCHEMICAL OXIDATION-REDUCTION
ENERGY STORAGE SYSTEM (NASA) 22 p HC A02/MF
A01 CSCL 10C

N78-14631

Unclas
55546

G3/44

ANION EXCHANGE MEMBRANES FOR ELECTROCHEMICAL OXIDATION-REDUCTION ENERGY STORAGE SYSTEM

Patricia M. O'Donnell, Dean W. Sheibley, and Randall F. Gahn
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

August 1977



Work performed as part of a joint effort with
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Energy Storage Systems
Under Interagency Agreement E(49-28)-1002

1 Report No NASA TM-73751	2 Government Accession No	3 Recipient's Catalog No	
4 Title and Subtitle ANION EXCHANGE MEMBRANES FOR ELECTROCHEMICAL OXIDATION-REDUCTION ENERGY STORAGE SYSTEM		5 Report Date August 1977	6 Performing Organization Code
		7 Author(s) Patricia M. O'Donnell, Dean W. Sheibley, and Randall F. Gahn	8 Performing Organization Report No E-9222
9 Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		10 Work Unit No	11 Contract or Grant No
		12 Sponsoring Agency Name and Address Energy Research and Development Administration Division of Energy Storage Systems Washington, D. C. 20545	
13 Type of Report and Period Covered Technical Memorandum		14 Sponsoring Agency Code Report No. ERDA/NASA 1002-77/2	
15 Supplementary Notes Prepared as part of a joint effort under Interagency Agreement E(49-28)-1002.			
16 Abstract Oxidation-reduction couples in concentrated solutions separated by appropriate ion selective membranes are an attractive approach to bulk electrical energy storage. A key problem is the development of the membrane. This report discusses four promising types of anionic membranes which were developed and evaluated for the Redox Energy Storage System. The copolymers of ethyleneglycoldimethacrylate with either 2-vinylpyridine or vinylbenzyl chloride gave stable resistance values compared to the copolymer of vinylbenzylchloride and divinylbenzene which served as the baseline membrane. A polyvinylchloride film aminated with tetraethylenepentamine had a low resistance but a high iron transfer rate. A slurry coated vinylpyridine had the lowest iron transfer rate. All these membranes functioned well in laboratory cells at ambient temperatures with the acidic chloride oxidant/reductant system. Fe III, Fe II/Ti III, Ti IV.			
17 Key Words (Suggested by Author(s)) Energy storage; Batteries; Electrochemistry; Membranes; Redox reactions		18 Distribution Statement Unclassified - unlimited STAR Category 44 ERDA Category UC-94c	
19 Security Classif (of this report) Unclassified	20 Security Classif (of this page) Unclassified	21 No. of Pages	22 Price*

**ANION EXCHANGE MEMBRANES FOR ELECTROCHEMICAL
OXIDATION-REDUCTION ENERGY STORAGE SYSTEM**

by Patricia M. O'Donnell, Dean W. Sheibley,

and Randall F. Gahn

Lewis Research Center

SUMMARY

Oxidation-reduction couples in concentrated solutions separated by appropriate ion selective membranes are an attractive approach to bulk electrical energy storage. A key problem is the development of the membrane. This report discusses four promising types of anionic membranes which were developed and evaluated for the Redox Energy Storage System. The copolymers of ethyleneglycoldimethacrylate with either 2-vinylpyridine or vinylbenzyl chloride gave stable resistance values compared to the copolymer of vinylbenzylchloride and divinylbenzene which served as the baseline membrane. A polyvinylchloride film aminated with tetraethylenepentamine had a low resistance but a high iron transfer rate. A slurry coated vinylpyridine had the lowest iron transfer rate. All these membranes functioned well in laboratory cells at ambient temperatures with the acidic chloride oxidant/reductant system, Fe III, Fe II/Ti III, Ti IV.

E-9222

INTRODUCTION

The current need for energy conservation has lead to investigations of various energy storage devices. One of the prime candidates as an energy storage system is the rechargeable electrochemical cell. Electrical energy is stored by conversion to chemical energy permitting extended periods of storage until the energy is required. An example

of electrochemical storage is the redox cell. Typically, a redox cell produces or stores electricity through the reversible oxidation and reduction of two solutions which are separated by an ion conductive membrane.

Although redox cells have been studied for many years, no practical applications have been made. Morrill (ref. 1) described a system which plated out in one half of the cell, but had soluble electrodes in the other side. Another version which also plates out like a conventional battery is a metal-halide cell (ref. 2). Mixed redox couples where the anolyte and catholyte share the same compartment are described in reference 3 and completely soluble systems in reference 4.

A new concept for the application of redox cells to bulk energy storage has been reported by Thaller (ref. 5). This concept differs from the previous ones since it utilizes a redox cell in which the electrodes are soluble and circulated continuously through the cell in both the charged and discharged state. The system consists of two electrolyte chambers containing inert electrodes separated by an ion selective membrane. The system is electrically rechargeable by reversing the current flow.

A schematic of the Redox Flow Cell is shown in figure 1 and the Power Conversion Section is shown in more detail in figure 2.

A vital part of this redox cell concept is the ionically conducting ion selective membrane. The function of the membrane is to prevent direct chemical reaction of the active electrochemical species so that they can react electrochemically in their respective compartments. At the same time the membrane must permit other ions to pass to maintain charge neutrality in the operating cell. Both cation and anion selective types of membranes are applicable. This designation refers to the predominant type of ion the membrane will allow to pass. Generally, membranes are crosslinked polymeric films that have small pores in them which are surrounded by charged sites. For very concentrated solutions, membranes with finely regulated pore sizes together with high concentrations of internal charges are required to make up for the partial loss

of Donnan exclusion brought about by the highly concentrated working solutions.

In the present work it was decided to maintain charge neutrality by transport of anions across an anion exchange membrane. This choice was made because it simplifies the reactant solution hydrogen ion management. Charge neutrality in an acidic system using a cation exchange membrane would be predominantly achieved by hydrogen ion transfer. Thus, a quantity of hydrogen ion equivalent to the number of electrons produced in the reaction must be transferred between the solutions. The constantly changing acidity is undesirable (ref. 5) especially so in highly concentrated salt solutions. A cation exchange membrane would also be a less effective separator for the active metal cations in the solutions. Transfer of an anion, such as chloride or sulfate for charge neutralization, causes no acidity change in either reactant solution. This is discussed in more detail in reference 5.

Preliminary screening of commercially available anion membranes indicated that vastly improved selectivity and resistivity characteristics were required for the Redox Flow Cell application. This paper describes the work up to December 1976 to develop a membrane with 20 Ω -cm resistivity, at least 10 000 hours with stable resistance and physical and chemical integrity, high selectivity, and a maximum production cost of <\$2.00 per ft².

EXPERIMENTAL METHODS

Evaluation Techniques

The experimental evaluation of the membranes was based on cation permeability, resistivity and cell performance.

The solutions used and their preparation are given in the appendix.

Permeability test. - Relative diffusion rates through the candidate membranes were measured by a colorimetric technique. A two compartment cell shown in figure 3 was used. The membrane was placed between the compartments and sealed to ensure no leakage. One side

was filled with 1 M FeCl_3 in 0.5N HCl and the other filled with 0.1N NH_4SCN in 0.5N HCl. Iron diffusing into the thiocyanate settles immediately to the bottom, spreads laterally and the red coloration of the $\text{Fe}(\text{SCN})_6^{-3}$ complex rises uniformly upward. Visual observation of the elapsed time following filling for the red coloration to half fill the thiocyanate side gave a relative comparison of the cation permeability of the membrane. Tests were run in duplicate. Variation between duplicate times ranged from 15 minutes in 1 hour to 1/2 hour in 6 hours.

Although this method is not a quantitative measure of diffusion rates, it was valuable in screening membranes for selectivity. The screening results correlated well with chemical analysis for crossover in operating cells even though the screening test did not have an applied electric-field.

Resistance measurements. - Since the output of an electrochemical cell is a function of its resistance, it is desirable to obtain a membrane with a minimum resistance. A redox flow cell like that shown in figure 2 was used for resistance measurements. The test membrane was clamped between the two halves with a gasket and a piece of graphite cloth on both sides. Each half of the cell was filled with the desired test solution. The resistance of the cell-membrane combination was measured using an AC bridge a 1 K Hertz. The total resistance, cell (carbon cloth inert electrodes and Grafoil current collectors) and membrane was measured. To obtain the membrane resistance alone a cell blank was determined. The blank was determined experimentally by two methods. In the first, a cell was assembled with all of the components except the membrane, filled with 6N HCl and the resistance measured. In the second method, cell resistances were measured with three, two and one membrane installed in the cell. By plotting the resistance versus the number of membranes, the cell blank resistance could be obtained by extrapolating back to zero number of membranes. Both methods agreed and a typical blank value was 0.10 Ω .

Resistance measurements were made using cells of the same design and identical internal structure. Measurements made with the AC bridge were accurate to $\pm 0.02 \Omega$.

Performance in cells. - The membranes for the Redox system must function adequately under a potential gradient. To test the membrane under dynamic conditions the same cell as shown in figure 2 was used with reservoirs of solutions and circulating pumps. Membrane and inert electrode area exposed to the solutions was 3.8 cm by 3.8 cm or 14.5 cm². Inert electrode material was Union Carbide WCA graphite cloth. The current leads were Union Carbide GTA Grafoil graphite tape. The tests were run using one ampere-hour (40 cm³) capacity of each solution (1M FeCl₃ in 0.5N HCl and 1M TiCl₃ in 6N HCl). Flow rates were between 10 and 20 cm³ per minute. The cells were cycled between fixed voltage limits. Cells were discharged through a constant load of 1 Ω to approximately 97 percent depth of discharge and then charged with a dc power supply to about 99 percent charge. The depth of charge/discharge was followed with an ampere hour integrator. A schematic diagram of the automatic cycling system is shown in figure 4. Test duration ranged from 300 to 700 hours.

In these tests, the effectiveness of the membranes as a separator was determined by the rate of cross diffusion of the two reactant solutions. Cross-diffusion of the anolyte and catholyte solutions, that is, Fe into the Ti solution and Ti into the Fe solution, was measured periodically by sampling and chemically analyzing each solution. The parameter determined in this test was $t_{\frac{1}{2}}$, the time for the iron solution of the redox test cell to lose one-half of its original concentration. This gives a good indication of the permselectivity of each membrane evaluated.

Results obtained for capacity loss due to cross-diffusion of solutions are averages of two determinations on all membranes except B2L-DT34A and DS156D.

Another method of continuously following the cross-diffusion of solutions during cycle tests was the measurement of the electrical amp-hour capacity of the system. Loss of active oxidizable or reducible species from their respective solutions is reflected in decreased amp-hour capacity. A dc amp-hour integrator electronically measured the current-time integral for a charge or a discharge. For the purposes of

this test, 50 percent more (in moles) Ti^{+3} than Fe^{+3} was used in the system. The system amp-hour capacity was therefore controlled by the Fe solution. Under these conditions the Fe^{+3} was completely reduced to Fe^{+2} on discharge and the Fe^{+2} was completely oxidized during charge. Thus the Fe remaining in the Fe solution was quantitatively determined by measuring the amp-hour capacity with the current time integrator. Continuous monitoring of the amp-hour capacity loss of the system indicated the rate of cross diffusion of the iron.

Membranes

Commercial materials. - Several commercially available anion exchange membranes were tested in the iron-titanium redox system using the method described in the EXPERIMENTAL section of this report. The only usable anion exchange membrane based on its life in the concentrated acid solutions was Ionics, Inc. 103QZL219, a copolymer of vinylbenzylchloride (VBC) and divinylbenzene (DVB) post reacted with trimethylamine (TMA). This membrane is a strong film, ~25 mils in thickness supported by Dynel fabric. The polymer network consists of a vinyl backbone crosslinked by a benzenoid structure and contains the strong base anion exchange group benzyltrimethylammonium chloride. This membrane was used as the standard against which the developmental membranes were compared. This baseline membrane, although functional, did not exhibit the characteristics required for a long life redox system when tested with the standard couples, iron-titanium. Its structure is shown in figure 5.

Developmental membranes. - To develop an improved anion membrane for long term redox applications, work was initiated in-house at the Lewis Research Center as well as under contract with Ionics, Inc. (ref. 8). The membrane development effort thus far has produced five promising membranes:

1. Ionics Inc. membranes - The chemical structures of the membranes studied are shown in figures 6 to 8.

The anion exchange membrane shown in figure 6 is a copolymer of vinylbenzylchloride and ethyleneglycoldimethacryate. This copolymer is then post aminated with diethylenetriamine. The compound contains both primary and secondary amines as exchange sites. The polymer is made incorporating a Dynel fabric for structural purposes. It is designated as B2LDT34A.

The chemical structure of the anion exchange membrane depicted in figure 7 is produced by aminating a polyvinylchloride film with tetra-ethylene pentamine. The exchange groups in this membrane are primary and secondary amines. It has been designated as VCITP12X.

The chemical structure of the anion exchange membrane shown in figure 8 is a copolymer of 2-vinylpyridine (2-VP) and ethyleneglycol-dimethacrylate. The membrane is cast on a Dynel fabric. The exchange group is a tertiary amine. The structure in figure 8 represents two types of membranes which are designated A3L28A and A4L28A. The difference between them resides in the amounts of 2-VP and EGDM reacted to form the copolymer. The A3L polymerization mixture contained 30 percent 2-VP and 36 percent EGDM whereas the A4L contained 37 percent 2-VP and 29 percent EGDM.

The membranes all contain a polymeric backbone to which is attached an amine functional group. The A3L and A4L membranes contain the amine functional group as a part of one of the reacting polymers. These membranes do not undergo post amination to introduce the amine functionality.

2. NASA-Lewis membrane - The in-house membranes utilized principles and technology developed for alkaline battery separators (ref. 7). These redox separator membranes are based on an organic-inorganic coating applied to a porous substrate. The coating materials consist of a stable nonreactive polymer in solution in a solvent. To this polymer solution, organic additives containing anion transport capability, and inorganic compounds possessing ion exchange or metal ion adsorption characteristics, are added. The volume percent of these additives range from 25 to 35 percent as calculated in the dry film. These mix-

tures are milled overnight in a porcelain ball mill to attain a uniform dispersion of fillers in the polymer as well as some reduction in particle size. The particular separator membrane studied in the present work (designated DS-156D) was made by applying two coats of the polymer dispersion to each side of 10 mil fuel cell grade asbestos sheet using factory coating equipment. The coating material consists of a Kraton G* polymer with crosslinked poly 4-vinylpyridine and magnesium zirconium silicate as additives. Approximately sixty formulations have been prepared with the Kraton rubber base material. The DS156 formulation was chosen because of its superior performance, but has not been optimized.

RESULTS AND DISCUSSION

The test results are all summarized in table I, the 103QZL219 served as the baseline membrane.

Permeability Results (Diffusion Time)

The permeability test results for the diffusion of ferric ion through each membrane gave an initial indication of the selectivity of the membrane to determine if additional testing was warranted. Comparison of the results shows that only the DS156D membrane was a significant improvement over the baseline membrane. DS156D is the slurry coated asbestos paper which acts like two membranes which could account for its lower rate of iron transport. The less selective membrane, VC1TP12X was included in this evaluation even though inferior to the baseline case to give a broader variety of membrane types and to demonstrate the capability of the testing methods.

*Kraton G; Shell Chemical Co., Houston, Texas

Resistance Measurements

Membrane resistance was evaluated in 6N HCl and 1M Fe⁺³, 0.5N HCl/1M Ti⁺³, 0.5N HCl environments under noflow conditions. The A4L28A VC1TP12X membranes have resistances in 6N HCl which are about one-third and one-fifth, respectively, of the baseline. Resistances in the static (noflow) redox environment were higher than in 6N HCl due to lower conductivity of the redox solutions. The A4L28A and VC1TP12X resistances were about 25 and 50 percent, respectively, less than the baseline. Reducing the membrane resistance plays an important role in decreasing the cell internal resistance. VC1TP12X has the lowest resistance in both acid and the redox environment.

Membrane resistivities which take into account the membrane thickness in 6N HCl are also given in table I and reflect the intrinsic properties of the membrane structure. The A4L28A showed the largest improvement over the baseline membrane. The DS156D and the B2LDT34A membranes were about the same as the baseline. The A3L28A and VC1TP12X also were an improvement over the baseline. Each of these values has been corrected for the cell blank.

Membrane Performance in Redox Cells

Membrane performance was evaluated under charge/discharge condition in the redox environment at room temperature. From these cycling tests the resistance stability of the membrane and the rate of solution cross-mixing under operating conditions was obtained.

A very important variable is the stability of the membrane resistance. At the beginning of this work a commercially available anion membrane could not be found which did not undergo a resistance change in the redox environment. The results obtained for the various membranes in this development program are shown in figure 9. The A4L28A and B2LDT34A membranes demonstrated stable resistances during more than 400 hours of cycle testing. This has been a major achievement in the development of a redox membrane. The baseline membrane had a

steadily increasing resistance as a function of time, which produced a corresponding decrease in cell voltage due to the increased IR losses. The DS156D and the A3L28A resistances increased about 10 percent in about 500 hours of cycle testing. The VC1TP12X resistance was the lowest and showed no increasing trend but fluctuated considerably. Subjective ratings for resistance stability are also given in table I.

Laboratory evaluation of separators produced in-house has shown that tertiary and secondary amines exhibit stable resistances over extended cycling time whereas the resistance of the quaternary amines increases with time. The contract membranes evaluated have shown much the same behavior on extended cycle testing.

Solution crossmixing, that is, the migration of the iron into the titanium and vice versa, decreases the amp-hour capacity of the system. As mentioned before, chemical analysis of the redox solutions and/or measurement of the amp-hour capacity electronically were used to determine the rate of crossmixing. The time for the system to lose one-half of its original capacity ($t_{\frac{1}{2}}$) was calculated by linear regression analysis of the iron solution concentration as a function of the square root of time. The results for crossmixing capacity are given in table I and also shown graphically in figure 10. Figure 10 also shows the good agreement between chemically and electronically measured amp-hour capacity for the A4L28A membrane.

The DS156 membrane exhibited the lowest rate of crossmixing (longest half time) and is in agreement with the result of the iron permeability tests. The VC1TP12X membrane had the shortest time to one half capacity which agrees with the permeability test. The B2LDT34A and A3L28A membranes fell in the middle in both tests. Only the A4L28A membrane gave a longer time to half capacity than would be predicted from the permeability test.

A qualitative measurement obtained from the cycling tests was the extent of solution movement through the membrane. A4L28A showed very small changes in solution volumes ($\sim 10\%$). The membrane allowing the largest change in volume was VC1TP12X which was ~ 25 percent.

These results indicate that there was preferential direction of movement of H_2O and/or HCl through the membrane.

The results obtained from the membrane developed specifically for redox application are improved over the best commercially available membrane, 103QZL219. It must be pointed out that no optimization was done on these membranes. Table II summarizes the progress that has been made since the development effort started and the goals thought to be required for a viable redox energy storage system.

CONCLUDING REMARKS

The anion membranes produced thus far (ref. 8) have much better characteristics than the available commercial membranes. They have been shown to be excellent candidates for use in the redox energy storage system. However, none of these new membrane types have been optimized in terms of the following: ion exchange capacity, water content, porosity, cross-link density or solvent content. The effect of improving these quantities on the performance of the membranes will be determined in further contractual and in-house efforts now in progress.

APPENDIX - SOLUTION PREPARATION**Iron III Chloride in 0.5N HCl**

Two liters of two molar stock solution was prepared by dissolving 1081.28 grams of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$) in about one liter of distilled water and 83.3 ml of 12N hydrochloric acid. The solution was filtered and diluted to final volume with water. One molar ferric chloride solutions were prepared by a 1:1 dilution of the two molar stock solution with 0.5N HCl. The stock solution was chemically analyzed for iron content.

Titanium III Chloride in 6N HCl

Two liters of two molar titanium stock solution was prepared by reacting 191.6 grams of technical grade titanium metal with two liters of 12N HCl in a 4 liter filter flask. The acid was heated to initiate the reaction and the titanium was added in two batches to control the reaction rate. A closed, trapped system was used to eliminate oxygen from the reaction flask. The solution was filtered and diluted to volume with water. One molar solutions were prepared by diluting the stock solution 1:1 with 6N HCl. The stock solution was chemically analyzed for titanium content. The titanium solution contained about 1.0 percent Fe impurity.

Ammonium Thiocyanate in 0.5N HCl

One half liter of 0.5M solution was prepared by dissolving 3.806 grams of ammonium thiocyanate salt in 0.5N HCl.

REFERENCES

1. Morrill, Joseph B.: Storage Battery Constituting a Closed System. U.S. Pat. 3,553,017, Jan. 1971.
2. Zito, Ralph: Metal Halide Battery. U.S. Pat. 3,642,538, Feb. 1972.
3. Kangro, W.: Verfahren Zur Steicherung Von Elektrischer Energie. D. B. P. 914264, July 1949.
4. Beccu, Klaus D.: Meeting Future Peak Electrical Energy Demands by Electrochemical Storage Systems. Chem. Ing. Tech., vol. 46, no. 3, 1974, pp. 95-99.
5. Thaller, L. H.: Electrically Rechargeable Redox Flow Cells. NASA TM X-71540, 1974. (Also see Paper 749142, 9th. Inter-Society Energy Conversion Engineering Conference, ASME, 1974, pp. 924-928.)
6. Warshay, Marvin and Wright, Lyle O.: Cost and Size Estimates for an Electrochemical Bulk Energy Storage Concept. NASA TM X-71805, 1975.
7. Sheibley, Dean W.: New Separators for Nickel-Zinc Batteries. NASA TM X-3465, 1976.
8. Alexander, S. S.; Geoffrey, R. R.; and Hodgdon, R. B.: Anion Selective Membrane. (Ionics, Inc.; NAS3-28897.) NASA CR 134931, 1975.

TABLE I. - SUMMARY OF TEST RESULTS

Membrane	103QZL219 (Baseline)	DS156D	A4L28A	A3L28A	B2LDT34A	VC1TP12X
Thickness, cm	0.063	0.047	0.070	0.069	0.065	0.021
Diffusion time, hr	5	24	5	5	3	1
Resistance in 6 NHCl, Ω^a	.34	.27	.12	.30	.28	.07
Volume resistivity in 6 NHCl, Ω cm	78	83	25	50	80	48
Resistance in static Fe/Ti, Ω^a	.50	.65	.35	.39	.50	.22
Crossmixing capacity loss. Time to 0.5 AH. ($t \frac{1}{2}$), hr ^b	980 1172 Av. 1076	2930	2050 1550 Av. 1800	780 810 Av. 795	1030	370 470 Av. 420
Resistance stability	Poor	Good	Excellent	Good	Excellent	Fair
Solution transfer	Fair	Good	Good	Fair	Fair	Poor

^a Values have been corrected for cell blank of 0.1 Ω .

^b Amp. hr capacity determined.

TABLE II. - SUMMARY OF MEMBRANE DEVELOPMENT

	2 Years ago	Now	Required
Operational membrane life	<24 hr	8000 hr	80 000 hr
Cell half life (crossmixing parameter)	150 hr	3000 hr	80 000 hr
Resistivity	200 Ω -cm	25 Ω -cm	10 Ω -cm
Resistance stabilized	<1 hr	1000 hr	80 000 hr

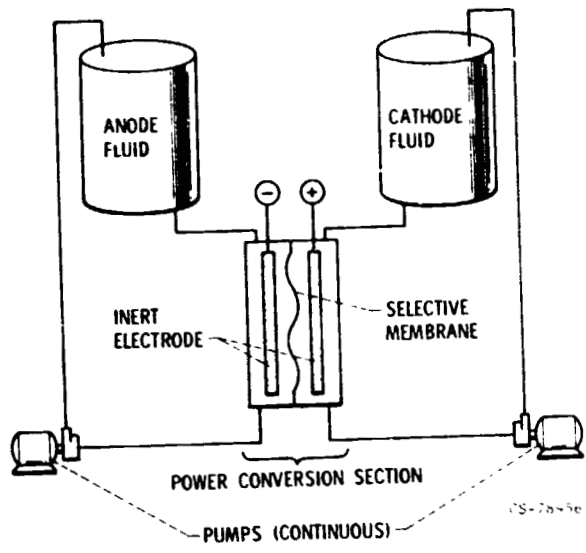


Figure 1. - Redox flow cell.

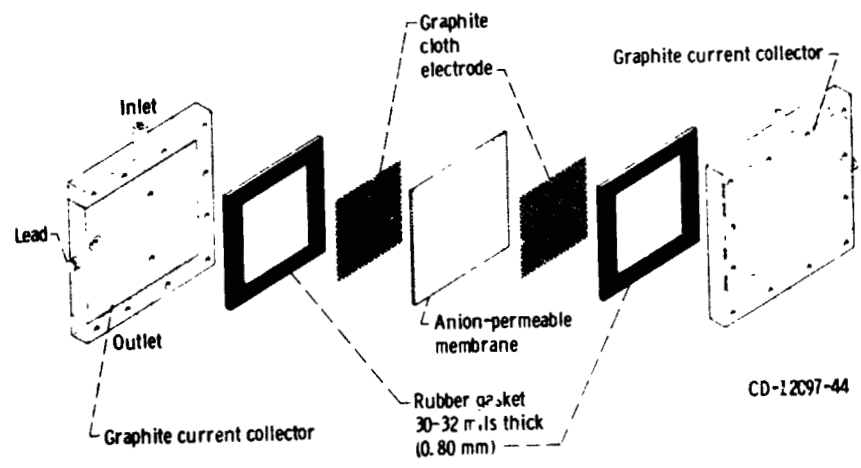


Figure 2. - Power conversion section.

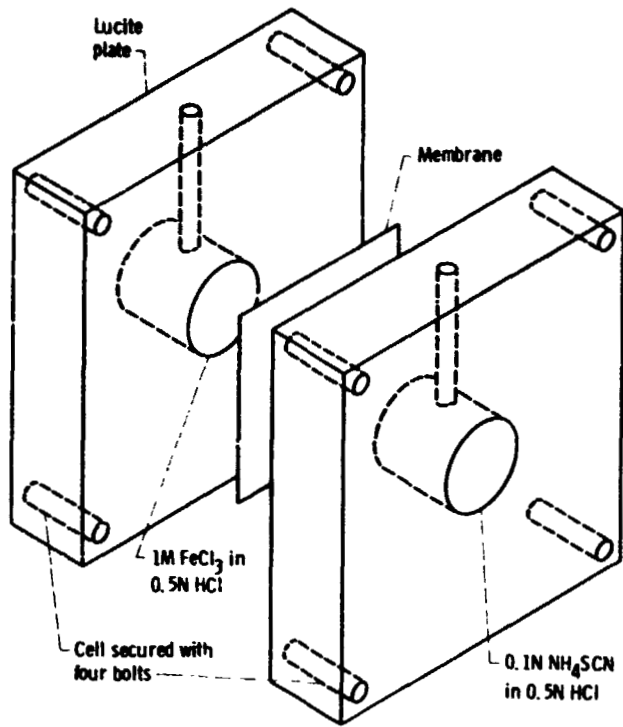


Figure 3. - Diffusion cell.

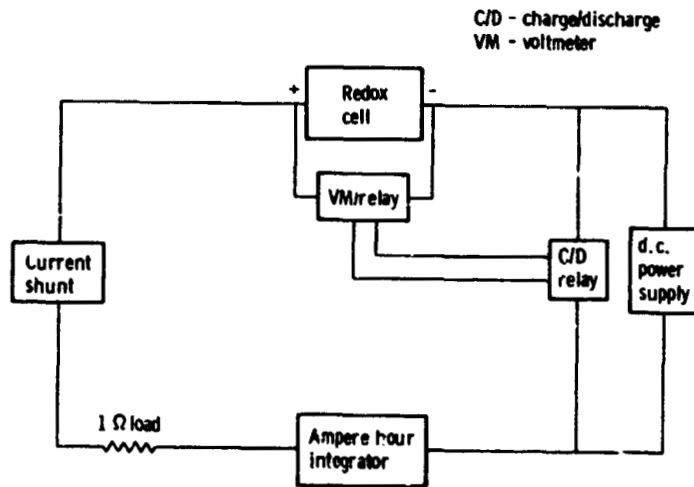


Figure 4. - Electrical schematic.

ORIGINAL PAGE IS
OF POOR QUALITY

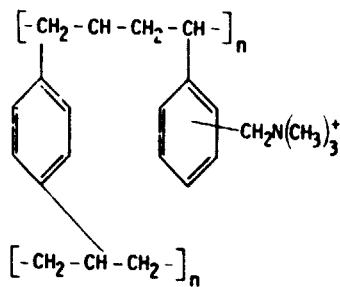


Figure 5. - 1030ZL219.

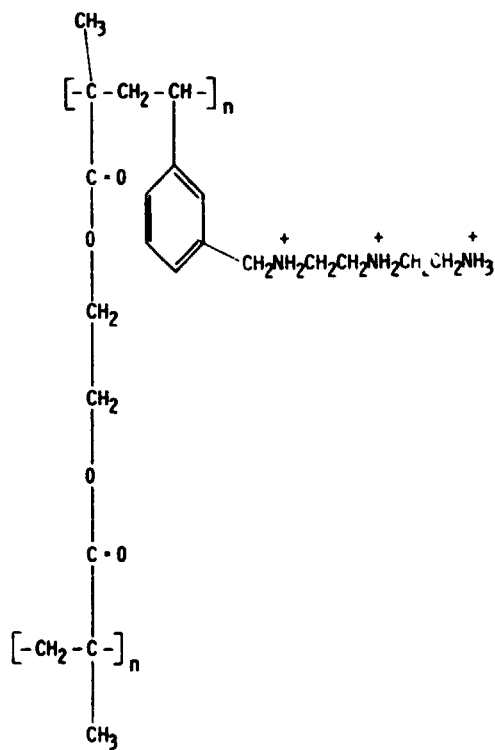


Figure 6. - B2LDT34A.

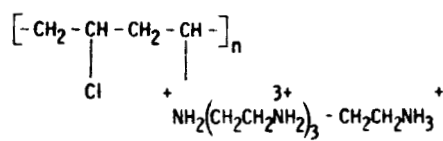
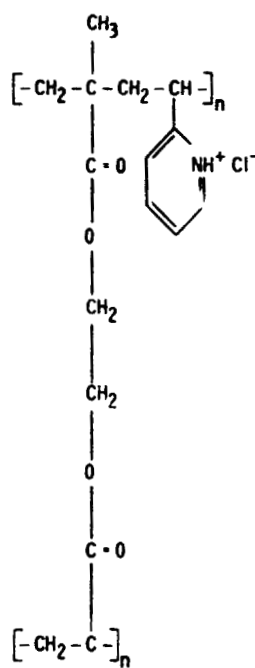


Figure 7. - VC1TP12X.



CH₃

Figure 8. - A4L-28A and A3L-28A.

ORIGINAL PAGE IS
OF POOR QUALITY

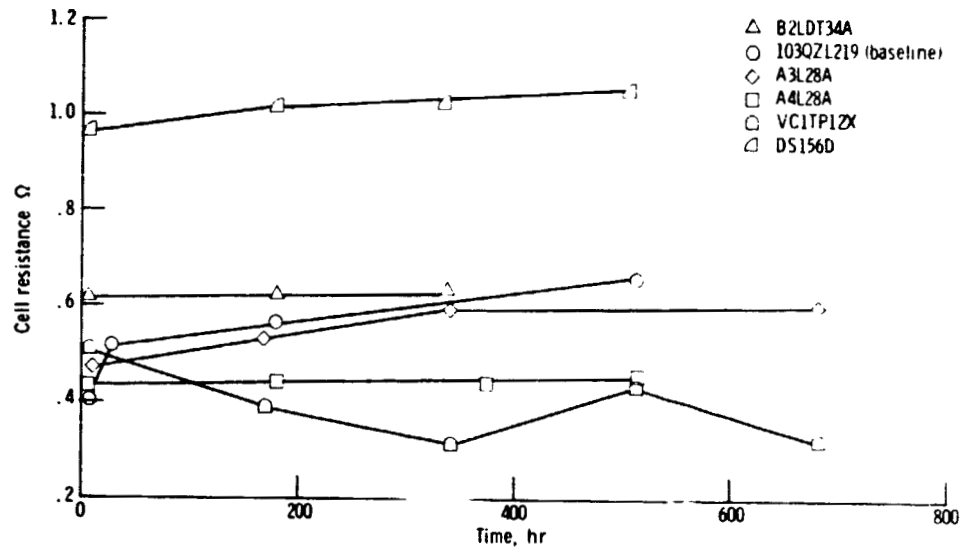


Figure 9. - Resistance studies on development membranes.

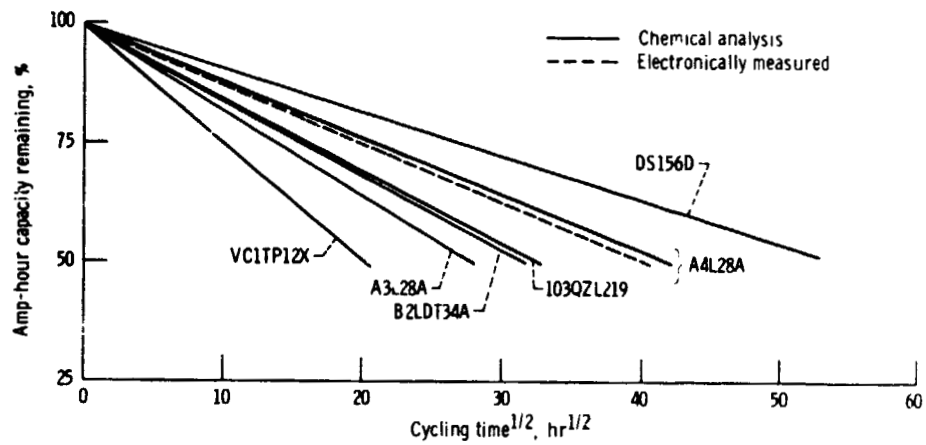


Figure 10. - Capacity loss of development membranes.