

ANION PERMSELECTIVE MEMBRANE

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ABS: Two polymer ion exchange membranes were synthesized to fulfill the needs
of both electrical resistivity and anolyte/catholyte separation for
utility load leveling utilizing the DOE/NASA mixed electrolyte REDOX
battery. Both membranes were shown to meet mixed electrolyte utility load
leveling criteria. Several modifications of an anion exchange membrane
failed to meet utility load leveling REDOX battery criteria using the
unmixed electrolyte REDOX cell.

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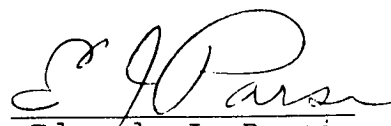
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A Final Report
Permselective Membranes
DEN 3-264

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FOREWORD

This document constitutes the final report for the work accomplished between March 1982 to May 1983 and October 1983 to May 1984 by Ionics, Incorporated for the National Aeronautics and Space Administration, Lewis Research Center, under Contract DEN 3-264 entitled Development and Preparation of REDOX Cell Anion Exchange Membranes.

Dr. Russell B. Hodgdon provided overall program management. The principal investigators were Samuel S. Alexander and Warren A. Waite.

Thanks are due to Ionics' R&D secretary for her patience in typing the final report manuscript and its many revisions.

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Introduction and Summary

This report, as was the case of our efforts in this actual contract, is in two distinct parts:

Part A: The development and testing of highly conductive-highly efficient anion exchange membranes to be used as the separator in the DOE/NASA REDOX iron-chromium battery for use in utility load levelling applications. The actual REDOX iron-chromium battery in this A part had complete separation of its iron and chromium chloride solutions and the membrane being developed to enable its use for utility load levelling has a requirement that its areal resistivity in 0.1N hydrochloric acid could not exceed 1.5 ohm-cm² and its ferric ion permeability must not exceed 5 micrograms of iron per cm² per hour in a one formal solution concentration variance of ferric chloride at pH = 0.

Part B: The development and testing of highly conductive-moderately efficient ion exchange membranes to be used as the separators in the NASA/DOE REDOX iron-chromium battery for use in utility load levelling applications. The actual REDOX iron-chromium battery in this B part has complete mixing of the iron and chromium chloride solutions and the membrane being developed to enable its use for utility load levelling has a requirement that its areal resistivity in 0.1N hydrochloric acid must be less than 1.0 ohm-cm² and its

ferric ion permeability should be a more feasible 1000 to 10000 micrograms of ferric ion per cm^2 per hour in a one formal solution concentration variance of ferric chloride at $\text{pH} = 0$.

Part A: Despite several testings of new chemistries to yield superconductive tight polyamine membranes of the CD1L type, Ionics was not able to achieve the objectives of preparing and testing a battery (REDOX Fe/Cr) separator capable of utility load levelling applications in this contractual effort.

- a) Several new, thin, non-woven backings were obtained and tested with the CD1L membrane type but none yielded the required low resistance-low iron permeability required for utility load levelling.
- b) The synthesis of the CD1L membrane was reversed to give excess reactive group to combine with polyamines in quest of very high ionic density membranes in acid solution. These membranes were not useful because of inherent pin hole leakage.
- c) Composite film CD1L membrane skins, plus skins of derivatives of the CD1L type membrane, were applied to macroreticular (1000Å pore) anion exchange membranes to give composite highly selective skin membranes having acid permeable centers. These were prepared in several combinations, some of which failed to yield composites, while others did not yield the combination of high-conductance coupled with low iron permeability that we

needed for utility load levelling.

- d) A low cost substitute for vinyl benzylchloride was found (Dichloroxylene) and a modified CDlL was prepared. No performance improvement over the standard CDlL was found.

In summary, no membrane variation of the standard CDlL membrane (an anionic co-polymer consisting of two unit formalites of dimethyl amino ethyl methacrylate with one unit formality of vinyl benzyl chloride in the finished polymerizate with pore volume of 27.5 non-polymerizeable) was found that would be capable of meeting utility load level applications in the fully separated Fe/Cr REDOX battery at 65°C in specified quantities of hydrochloric acid and the metal halides.

Ionics now believes that the creation of a fabric backed anion exchange membrane capable of ALL applications in the specified iron/chromium REDOX battery (metal reactants fully separated) at 65°C is highly improbable, although the CDlL membrane may be suitable for some specific applications.

Part B: DOE/NASA, in mid-1982, developed the mixed electrolyte iron-chromium REDOX battery with a far less stringent metal ion permeability requirement than the fully separated metal ion type. Here, separation of variable charged metallic types was desirable but not the separation of the metallic ion species themselves. Resistivity thus became a key to this battery separator rather than the tough combined resistivity-permeability requirement.

Ionics developed two distinct REDOX (mixed electrolyte) battery separators which were synthesized and tested and found to be candidates for the REDOX battery's use as a utility load levelling device. The task of membrane synthesis became different when permeabilities of ~ 1000 micrograms of iron per cm^2 per hour per unit molarity became tolerable. This allowed very thin, highly conductive structures to be synthesized without the use of fabric backings.

Two types of ion exchange membranes were synthesized, prepared as membrane structures, and tested. These met utility load levelling requirements and are presently under test at the NASA-LEWIS Research Center.

The Cation Exchange "CPS" Membrane Separator

One membrane prepared was of the sulfonic cation type, and is mechanically very strong. The membranes were designated the "CPS" series and were submitted to DOE/NASA with the following qualifications:

1. Resistivity < 1.0 ohm-cm² in 0.1N HCl.
2. Permeability ranges from 50 to 7700 $\mu\text{gFe}^{+3}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$ with higher permeability numbers being capable of running at high current densities.
3. Membranes capable of being prepared and supplied in the 3 to 7 mil thickness range without fabric backing.
4. Membranes stable in cell operation for long term testing at 65°C with no operating loss.
5. Membranes undergoing failure can be repaired or reformed into new membranes.
6. Membrane systems above modifiable for optimum properties.

The Cation Exchange "CPS" membrane types meet utility load levelling applications with the mixed electrolyte REDOX iron-chromium battery and have demonstrated long life.

The Anion Exchange "VCTP" Membrane Separator

One membrane prepared was of the weakly ionized polyamine anion exchange type which is mechanically very strong.

The membranes were designated the "VCTP" series and have been submitted to DOE/NASA with the following qualifications:

1. Resistivity < 1.0 ohm-cm^2 in $0.1N \text{ HCl}$.
2. Permeability ranges from 4150 to 11700 $\mu\text{gFe}^{+3}/\text{cm}^2/\text{hr}/M/L$.
3. Membranes capable of being prepared and supplied in the 3 to 7 mil thickness range without fabric backing.
4. Membranes stable in iron chloride at 65°C for several hundred hours to date.

The anion exchange "VCTP" membrane type meet utility load levelling applications with the mixed electrolyte REDOX iron-chromium battery and have demonstrated long life.

Developmental Results

Part 1. Membrane Separators for the DOE/NASA Mixed Electrolyte REDOX Battery

Contract DENS 3-264 is a continuation of the work at Ionics, Inc. to synthesize and evaluate ion permselective membranes that are useful as battery separators in a REDOX storage battery being developed at the NASA Lewis Research Center. Because of the recent conversion by NASA to the mixed Fe, Cr battery electrolyte, the laboratory effort has been directed toward the utilization and synthesis of permselective membranes having higher porosities and electrolyte cross diffusion than was permitted in the previous REDOX battery configuration of separate Fe and Cr solutions.

The goals for candidate permselective membrane properties suitable for the mixed electrolyte battery were:

- Low electrical resistivity - below $1 \Omega\text{-cm}^2$ in 0.1N HCl.
- Membrane porosity as measured by Fe^{+3} diffusion not established but estimated in range of 10^3 to 10^4 $\mu\text{gFe/cm}^2\text{/hr/M/L}$.
- Long term physical and chemical stability in REDOX environment at 65°C .

- Long term operational stability (i.e., stable resistivity and cell efficiency).
- Good potential in synthesis process for optimization of membrane.
- Ease of manufacture.
- Low cost of membrane.

Anion and cation membrane candidates were synthesized which showed good potential for use in the new mixed electrolyte REDOX battery system.

- Cation membrane CPS, an unbacked highly conductive film, has shown excellent stable performance characteristics in the REDOX cell at 65°C for over 700 hrs. operating time. No change was reported in the operational parameters of current efficiency, low electrical resistivity and physical durability. Other noteworthy features of the CPS membrane were ruggedness to temperature cycling stress, low cost and ease of manufacture, and availability in a wide range of porosities.
- Another membrane candidate was the unbacked anion membrane VCTP. The VCTP membrane also gave low electrical resistivities, low cost and ease of manufacture in a number of different porosities in the acceptable range of Fe diffusivities.

11.1.A. UNBACKED CATION EXCHANGE MEMBRANES FOR MIXED METAL
ION REDOX BATTERY

Cation Membranes CPS

The CPS cation membranes is a thin unbacked highly conductive polymeric film composed of an acid-and oxidation-resistant backbone and sulfonic acid ion exchange groups. The membrane was prepared by solvent casting. Casting produced physically strong pinhole-free films up to 1.5 ft² in area and 4 to 8 mils in thickness. A wide range of film gauge can be obtained.

Five different membrane samples 4-7 mils in thickness were delivered to NASA Lewis for REDOX battery evaluation. These represented a range of ion exchange capacities (IEC) from 0.88 to 2.67 meq per dry gram resin and water contents of 34 to 67.5% (Wet Basis). The electrical resistivities (R_p) in 0.1N HCl at room temperature were all less than 1.0 Ω -cm² and the film porosities as measured by diffusion of Fe⁺³ were 50 to 7700 μ gFe/cm²/hr/M/L (Table I).

TABLE I

PROPERTIES OF CPS UNBACKED CATION MEMBRANES

| ID | GAUGE (MILS) | RESISTIVITY IN 0.1N HCL (OHM-CM ²) | H ₂ O CONTENT (%) | IEC (MEQ/DGR) | INTERSTITIAL MOLALITY (M/L) | DIFFUSION RATE (μ GFE/ CM ² HR M/L) |
|-------|-----------------|--|---------------------------------|------------------|-----------------------------------|--|
| CPS-1 | 4 | 0.55 | 67.5 | 2.67 | 1.28 | 7,700 |
| CPS-2 | 5 | 0.65 | 65.3 | 2.30 | 1.22 | 1,670 |
| 9039 | 5 | 0.44 | 64.0 | 2.16 | 1.21 | 912 |
| 99 | 3.5 | -- | 48.2 | 1.81 | 1.95 | 773 |
| 1959 | 4 | 0.90 | 34.0 | 0.88 | 1.69 | 50 |

NASA Lewis tests have demonstrated that CPS membranes have long term physical durability and stable functional properties in the REDOX environment. Membrane CPS-99 has given over 700 hrs. of REDOX cell operation at 65°C with no apparent change in cell resistivity or performance. In these tests the membranes have also endured repeated temperature cycling from ambient temperature to 65°C without physical deterioration as can occur with membranes containing fabric backing material. The CPS membrane series also provided the REDOX battery system with a wide range of optimum current densities of 40 to 150 mA/cm² at coulombic efficiencies of 91 to 93% and energy efficiencies of 76 to 86%.

The fabrication of the CPS membrane is a film casting process and has the potential for the manufacture of large continuous membrane areas. Any scrap can be reprocessed into usable membranes.

Properties of the CPS membrane can be modified by conditions of manufacture and post treatment of the film.

Summary - CPS membrane

- Low resistivity
- Good REDOX battery performance at 65°C
- Long term physical and electrochemical stability
- Durable in thermal stress environment
- Usable in wide range of current density conditions
- Good potential for property modification
- Low cost and ease of manufacture

Most Important - capable of meeting utility load levelling applications in the DOE/NASA iron-chromium mixed electrolyte REDOX battery.

II.1.B. UNBACKED ANION EXCHANGE MEMBRANES FOR MIXED
METAL-ION REDOX BATTERY

Anion membrane VCTP

Anion membrane VCTP is an unbacked high conductivity permselective film composed of an acid and oxidation resistant backbone and pendant weakly basic polyalkyl amine hydrochlorides as the ion exchange groups. The VCTP samples were physically strong, pinhole-free films with ion exchange capacities of 1.60 to 4.43 milliequivalents per dry gram membrane and Fe diffusivities of 4150 to 11,700 $\mu\text{gFe}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$. The electrical resistivity in 0.1N HCl for all samples was less than 1 $\Omega\text{-cm}^2$ at ambient temperature.

Post treatment of the VCTP membrane at elevated temperature in FeCl_3 solution resulted in a substantial decrease of film porosity with only a small increase in resistivity (Table III). Immersion of a membrane in 1M FeCl_3 , 3N HCl solution at 65°C for 64 hrs. reduced the Fe diffusion from 4150 to a stable level of 1390 $\mu\text{gFe}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$ and showed a very small rise in R_c of 0.5 to 0.64 $\Omega\text{-cm}^2$ (Fig. 1).

The VCTP membrane can be readily manufactured in dimensions up to 54 inches wide and 1-8 mils in thickness.

TABLE II

PROPERTIES, VCTP MEMBRANES

| SAMPLE NO. | REACTION TIME AMINE (HRS.) | IEC (MEQ/DGM) | H ₂ O CONTENT (%) | RESISTIVITY ¹ R_0 (Ω - CM ²) | FE DIFFUSION ² D_{Fe_2} (μ CFe/CM HRM/L) |
|---------------|-------------------------------------|----------------------------|------------------------------------|---|--|
| 1 | 4.5 | 3.23 | 29.1 | 0.6 | 4150 |
| 2 | 6.0 | 3.85 | 33.4 | 0.5 | 4980 |
| 3 | 2.5 | 1.60 | 41.3 | 0.86 | 4670 |
| 4 | 3.75 | 3.29 | 49.0 | 0.62 | 11,700 |
| 5 | 4.5 | 4.04 | 37.4 | 0.5 | 8090 |
| 6 | 6.0 | 4.43 | 47.8 | 0.5 | 8890 |
| 7 | 22 | FRANGIBLE, TEARS EASILY -- | | | --- |

¹ Resistivity measured with contact probes in 0.1NHCl.

² Fe Diffusion solutions, 1MFeCl₃, 0.5NHCl vs. 2MCaCl₂, 0.5NHCl.

TABLE III

PROPERTIES OF VCTP UNBACKED MEMBRANES -
POST TREATED IN FeCl_3 3N HCL SOLUTION

TEMP. 65 C

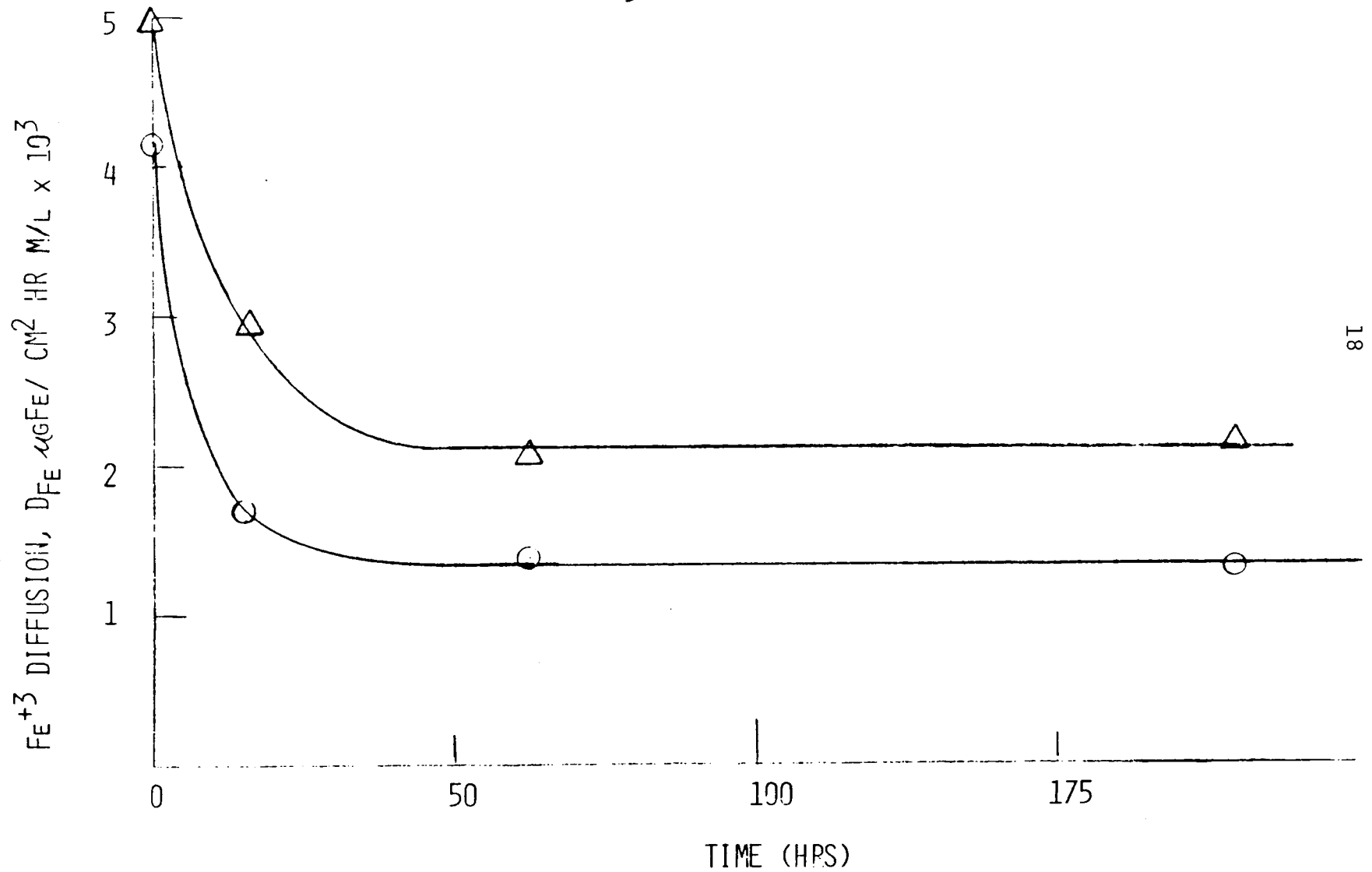
| <u>SAMPLE NO.</u> | <u>TIME IN SOLUTION (HR)</u> | <u>FE DIFFUSION ($\mu\text{GFE}/\text{CM}^2\text{HRM/L}$)</u> | <u>RESISTIVITY¹ R ($\Omega\text{-CM}^2$)</u> |
|-------------------|--------------------------------------|--|--|
| 1 | 0 | 4150 | 0.52 |
| | 16 | 1690 | -- |
| | 64 | 1390 | 0.64 |
| | 180 | 1310 | -- |
| 2 | 0 | 4980 | 0.52 |
| | 16 | 2940 | -- |
| | 64 | 2070 | 0.62 |
| | 180 | 2140 | -- |

¹ Resistivity measured with contact probes in 0.1N HCl.

² Fe Diffusion solutions, 1M FeCl_3 , 0.5N HCl vs. 2M CaCl_2 , 0.5N HCl.

FIGURE 1

ANION MEMBRANE VCTP - POROSITY AS A FUNCTION OF CONTACT TIME IN
1MFE CL_3 , 3NHCL AT 65°C



This membrane can be easily fabricated in a one step reaction process from low cost raw materials.

Variables in the synthesis of the VCTP anion permselective membrane are the amination temperature, time of reaction, amine species, and thickness of the film.

Post treatment variables are time, temperature and composition of the treatment solution.

Summary - VCTP Anion Membrane

- Thin strong film
- Low electrical resistivity
- Porosities in the acceptable range
- Good potential for modification of properties by synthesis or post treatment
- Ease of manufacture
- Low cost of manufacture
- Ready availability of raw material

Most Important - Capable of meeting utility load levelling applications in the DOE/NASA iron-chromium mixed electrolyte REDOX battery.

TABLE IV

PROPERTIES OF VARIOUS ANION MEMBRANE VCTP
AS A FUNCTION OF
REACTION TIME

FILM THICKNESS - 2 MIL

AMINATION TEMP. - 65°C

| <u>FILM NO.</u> | <u>REACTION TIME (HRS.)</u> | <u>RESISTIVITY, R_e IN 0.1NHCl (Ω-CM²)</u> | <u>Fe DIFFUSION D_{Fe} μgFe/CM²/HR/M/L</u> |
|---------------------|-------------------------------------|--|--|
| 253 | 2 | 0.91 | 5477 |
| | 3 | 0.81 | 9113 |
| | 4 | 0.71 | -- |
| | 6 | 0.64 | -- |
| 254 | 2 | 0.84 | 8341 |
| | 3 | 0.79 | 9565 |
| | 4 | 0.66 | -- |
| | 6 | 0.58 | -- |
| 255 | 2.5 | 0.86 | 4670 |
| | 3.8 | 0.50 | 8090 |
| | 4.5 | 0.50 | 8890 |
| | 6.0 | 0.62 | 11,700 |

Summary and Conclusions: (Part 1)

The discovery by DOE/NASA that the mixed electrolyte REDOX battery was feasible has led to the creation of two membrane separators, one cation exchange for H_3O^+ , one anion exchange for Cl^- to complete battery circuitry which meet the needs of utility load levelling. Both are simple to make and of low end cost.

II.2.C. MEMBRANE SEPARATORS FOR THE DOE/NASA SEPARATED ELECTROLYTE REDOX BATTERY

Backed Cation Exchange Membranes

A number of cation exchange membranes were prepared and screened for resistance and selectivity. These were made on standard and special fabrics. They were evaluated to assess the effects of various backings on the iron selectivity and on the electrical resistivity criteria. Some results of this screening can be found in Table V. Comparison, on the basis of ion exchange capacity, between cation and anion exchange types highlight their differences. For instance, the W285-56, a cation exchange membrane (IEC 2.20), has a resistance ($2.1 \Omega\text{-cm}^2$), much lower than the W285-57, a comparable medium capacity (IEC 2.34) anion exchange membrane ($4.9 \Omega\text{-cm}^2$). The cation membrane also has better iron selectivity.

Several cation exchange membranes were found having resistances below one ($1.0 \Omega\text{-cm}^2$) in 0.1N HCl. Thin fabric membranes of this type however generally exhibited a considerable number of minute pinholes or evidenced incomplete saturation. Usually the woven fabrics had pinholes while the non-wovens tended to show blisters.

Several base CR-62 membranes were checked on the reference woven modacrylic backing and additionally on a woven polyester, a woven

TABLE V

MEMBRANE SCREENING
CATION AND ANION TYPES

| <u>Designation</u> | <u>Type</u> | <u>Backing Fabric</u> | <u>0.1N HCl Resistance</u> | | <u>% Water</u> | <u>Ion Exchange Capacity meq/gdr</u> | <u>Selectivity 1M FeCl₃-1N HCl μg Fe/hr/cm²/mol/l</u> | |
|--------------------|-----------------------------|------------------------------|--------------------------------|-----------------------------|--------------------|--|---|--------|
| | | | <u>(t,cm)</u> | <u>R = Ω-cm²</u> | | | | |
| W 285-56 | Cation | Woven Modacrylic | 0.055 | 2.1 | 39.0 | 2.20 | 151 | (201*) |
| W 285-57 | Medium Capacity Anion | Woven Modacrylic | 0.055 | 4.9 | 45.8 | 2.34 | 314 | |
| MT 281-89 | Cation | Woven Polypropylene | 0.025 | 1.7 | 34.3 | 2.37 | 49.6 | |
| MT 281-100 | Cation | Woven PVC | 0.11 | 0.86 | (30 NP) | 2.3*** | 166 | |
| | Cation | Non-Woven Polyester** | | -- | (30 NP) | 2.3*** | 116 | |
| | Cation | Non-Woven Glass** | | -- | (30 NP) | 2.3*** | 107 | |
| Typical Control | CDLL Anion | Woven Modacrylic | 0.040 | 4.3 | 33.7 | 4.22 | 35 | |

* 0.5 N HCl, 1M FeCl₃/0.5 N HCl

** Incomplete saturation

*** Typical value

polyvinylchloride and a woven polypropylene backing. One system was also checked on a non-woven glass fabric.

The results of this set of tests are listed in Table VI. The W285-64A and W285-64C formulations were prepared in the usual manner and a number of fabrics impregnated. The acid post-treatment of these boards destroyed the thin woven polyester fabric. The other backings survived reasonably well, the woven polyvinylchloride yielding one of the better membranes. The cation membrane made on non-woven glass fabric had good conductivity, however, it tended to crack on handling.

Other backed cation membranes were fabricated without acid post-treatment. These membranes had varying NP contents and were made on a woven modacrylic, a non-woven modacrylic and a fine woven polyester.

Table VII lists the results of these screening tests. Generally speaking, the fabrication of high quality, leak free membranes occurred most readily and most consistently on the woven and the non-woven modacrylic fabrics.

The lowest resistances were measured on membranes backed with the non-woven modacrylic fabric and with the very thin woven polyester fabric. In a general way, increased NP content yielded membranes with lower resistance and poorer selectivity. The woven polyester

TABLE VI
MEMBRANE SCREENING
CATION TYPES

| <u>Designation</u> | <u>Backing Fabric</u> | <u>Leak Test</u> | <u>(t, cm)</u> | <u>R = Ω-cm²</u> | <u>% Water</u> | <u>Ion Exchange Capacity meq/gdr</u> | <u>Selectivity 1M FeCl₃-1N HCl μg Fe/hr/cm²/mol/l</u> |
|-----------------------|-----------------------|------------------|----------------|---|----------------|--|--|
| W285-64A | Woven Modacrylic | OK | 0.055 | 1.7 | 44.8% | 2.92 | -- |
| | Woven Polyester | Poor | | Disintegrated In Processing | -- | -- | |
| | Woven Vinyl Chloride | OK | 0.015 | 1.48 | -- | -- | 539 |
| | Woven Polypropylene | Fair | 0.024 | 1.8 | -- | -- | 744 |
| W285-64C | Woven Modacrylic | OK | 0.055 | 1.8 | 38.6% | 2.61 | -- |
| | Woven Polyester | Poor | | Disintegrated In Processing | | -- | -- |
| | Woven Vinyl Chloride | OK | 0.015 | 1.64 | -- | -- | 371 |
| | Woven Polypropylene | Fair | 0.025 | 1.8 | -- | -- | -- |
| MT306-05 (W285-67) | Non-Woven Glass | Fair | 0.016 | 0.74 | -- | -- | 146 (Edges Cracked) |

TABLE VII
MEMBRANE SCREENING
CATION TYPES

| <u>Designation</u> | <u>Type</u> | <u>Backing Fabric</u> | <u>Leaks</u> | <u>(t,cm)</u> | <u>R = Ω-cm²</u> | <u>% Water</u> | Ion Exchange Capacity | Selectivity 1M FeCl ₃ -1N HCl |
|-----------------------|----------------------|--------------------------------------|--------------------------|---------------|---|--------------------|--------------------------|---|
| | | | | | | | <u>meq/gdr</u> | <u>μg Fe/hr/cm²/mol/l</u> |
| 285-87 A (V195-83) | High NP | Woven Modacrylic | OK | 0.045 | 1.48 | 37.5 | 2.72 | 151 |
| | High NP | Fine Woven Polyester | Fair | 0.010 | -- | -- | -- | 271 |
| 285-87 B | Low NP | Woven Modacrylic | OK | 0.045 | 1.84 | 35 | 2.28 | 89.5 |
| 285-89 (V195-xx) | MOD NP | Non-Woven Modacrylic | OK | 0.032 | 0.90 | -- | -- | 97.4 |
| 285-94 | Very High NP (50) | Woven Modacrylic | OK | 0.052 | 1.1 | -- | -- | -- |
| | | Fine Woven Modacrylic | Fair | 0.039 | 1.0 | -- | -- | -- |
| | | Fine Woven Polyvinyl- chloride | Fair | 0.009 | 0.75 | -- | -- | -- |
| | | Fine Woven Polyester | Fair | 0.008 | 0.5 | -- | -- | -- |
| As Above | Very High NP (45) | Woven Modacrylic | OK | 0.044 | 1.2 | -- | -- | 199 |
| | | Non-Woven Modacrylic | OK slight blisters | 0.024 | 0.9 | -- | -- | 497 |
| | | Fine Woven Polyester | Fair | 0.009 | 0.6 | -- | -- | 1,024 |
| | | Fine Woven Polyvinyl- chloride | Fair | 0.010 | 1.0 | -- | -- | 455 |

fabric was thin and gave the best conductivity values, however, its selectivity was only fair, and considerable difficulty was experienced in consistently producing high quality membranes.

A number of these cation exchange membranes backed with woven and non-woven fabrics were sent to the NASA REDOX Group for their examination and evaluation.

II.2.D. COMPOSITE MEMBRANES

A series of "membrane boards" were prepared with high N.P. contents (50 to 60 NP). Sets were prepared having terminal active amine, terminal active chloride or terminal active oxirane groups. These sets of boards had the following composition:

- a) 2 moles of DMAEMA and 1 mole of EGDM to yield a board with terminal active amine.
- b) 2 moles of VBC and 1 mole of DMAEMA to yield a board with terminal active chloride.
- c) 2 moles of GMA and 1 mole of EGDM to yield a board with terminal active oxirane ring.

These boards were treated with appropriate monomers, unpolymerized CDLL solution, polymer solutions, and polyamines. Many of the monomer and polymer solutions plugged the surface and while reducing permeability substantially, increased the resistance of the membranes to unacceptable levels.

The use of specific solutions and reactants also was explored. These materials generally reacted with the pendant groups as expected. These reactions were indicated by substantial

TABLE VIII

Treatment vs. Resistivity
 50 NP "Board" - Active Amine
 Polymer - 2 Mole DMAEMA/Mole EGDM

| <u>Treatment</u> | <u>Thickness</u> (cm) | <u>Resistivity</u> 0.01N NaCl (Ω -cm ²) | <u>Resistivity</u> 0.1N HCl (Ω -cm ²) |
|---------------------------|--------------------------|---|---|
| Control No treatment | 0.055 | 95.9 | 4.1 |
| Meta-DCX (High purity) | 0.55 | 21.7 | 9.2 |
| 75/80% <i>m</i> -DCX | 0.061 | 21.7 | 7.4 |
| Poly VBC (one coat) | 0.062 | 1414 | 154 |
| Poly VBC (two coats) | 0.070 | 3070 | 160 |
| VBC Monomer | 0.054 | 1600 | 17.2 |
| 5% Para DCX* | 0.054 | 92.3 | 4.3 |
| Epoxy Resin | 0.046 | 492 | 9.8 |

* Para DCX

α α' - Dichloro-*p*-xylene

TABLE IX

Treatment vs. Resistivity
 50 NP "Board" - Active Chloride
 Polymer - 2 Mole VBC/1 Mole DMAEMA

| <u>Treatment</u> | <u>Thickness</u> (cm) | <u>Resistivity</u> <u>0.01N NaCl</u> (Ω -cm ²) | <u>Resistivity</u> <u>0.1N HCl</u> (Ω -cm ²) |
|-----------------------------|--------------------------|--|--|
| No treatment Control | 0.055 | 14.7 | 5.9 |
| One Coat Poly DMAEMA | 0.055 | 18.5 | 5.9 |
| Two coats Poly DMAEMA | 0.061 | 13.5 | 5.9 |
| DMAEMA Monomer | 0.055 | 13.5 | 6.8 |
| Tetraethylene- pentamine | 0.056 | 12.9 | 4.1 |
| Polyglycol- diamine | 0.058 | 13.5 | 5.3 |
| CD1L Coating | 0.061 | -- | 6.1 |

TABLE X

Treatment vs. Resistivity
 50 NP "Board" - Active Oxirane
 Polymer - 2 Mole GMA/1 Mole EGDM

| <u>Treatment</u> | <u>Thickness</u> (cm) | <u>Resistivity</u> <u>in 0.01N NaCl</u> (Ω -cm ²) | <u>Thickness</u> (cm) | <u>Resistivity</u> <u>in 0.1N HCl</u> (Ω -cm ²) |
|-----------------------------|--------------------------|---|--------------------------|---|
| No treatment Control | 0.052 | 221 | 0.054 | 13.0 |
| Diethylene- triamine | 0.058 | 289 | 0.058 | 4.9 |
| Ethylene- diamine | 0.058 | 160 | 0.062 | 3.9 |
| Tetraethylene- pentamine | 0.058 | 268 | 0.058 | 5.5 |
| Triethylene- tetramine | 0.056 | 264 | 0.062 | 3.4 |
| Polyglycol- diamine | 0.053 | 246 | 0.058 | 9.2 |

GMA = Glycidyl Methacrylate

TABLE XI

MEMBRANE SCREENING
NON-VBC ANION TYPES

| <u>Designation</u> | <u>Type</u> | <u>Backing Fabric</u> | <u>(t,cm)</u> | <u>R = Ω-cm²</u> | <u>% Water</u> | <u>Ion Exchange Capacity</u> | <u>Selectivity</u> 1M FeCl ₃ -1N HCl |
|--------------------|---|---------------------------|--------------------|---|--------------------|----------------------------------|---|
| | | | | | | <u>meq/gdr</u> | <u>μg Fe/hr/cm²/mol/l</u> |
| W285-74A | 1M DVB/ 2M DMAEMA 40 NP | Woven Modacrylic | 0.059 | 4.1 | -- | -- | -- |
| | | Woven Polyester | 0.011 | Leaks | -- | -- | -- |
| | | Woven Vinyl | 0.021 | 9.7 | -- | -- | -- |
| W285-74C | 1M DVB/2.5M DMAEMA 40 NP | Woven Modacrylic | 0.062 | 3.9 | -- | -- | -- |
| | | Woven Polyester | 0.010 | Leaks | -- | -- | -- |
| | | Woven Vinyl | 0.021 | 9.0 | -- | -- | -- |
| W285-76D | 1M DVB/ 2M DMAEMA 35 NP Early Cat. | Woven Modacrylic | 0.045 | 3.8 | -- | -- | -- |
| | | Woven Polyester | 0.012 | 1.8 | -- | -- | -- |
| | | Woven Vinyl | 0.018 | 8.4 | -- | -- | -- |
| W285-76E | 1M DVB/ 2M DMAEMA 35NP Late Cat. | Woven Modacrylic | 0.044 | 2.9 | -- | -- | -- |
| | | Woven Polyester | Massive Leaking | | | -- | -- |

TABLE XI (A)

| | | | | | | | |
|----------|--|---|-------|------|------|------|----------------|
| W285-77F | 1M DVB/ 2M DMAEMA 35NP Presoak | Woven Modacrylic | 0.054 | 5.4 | 34.4 | 3.27 | 133 |
| | | Woven Polyester | 0.010 | 2.3 | -- | -- | 465 |
| | | Woven Vinyl | 0.018 | 4.0 | -- | -- | -- |
| W285-77G | 1M DVB/ 2M DMAEMA 35 NP Butanol | Woven Modacrylic | 0.049 | 4.8 | 33.0 | 3.30 | 76.2 |
| | | Woven Polyester | 0.011 | 4.5 | -- | -- | 282 |
| | | Woven Vinyl | 0.018 | 4.0 | -- | -- | -- |
| | | Glass/ Polyester | 0.013 | 3.2 | -- | -- | 289 |
| W285-77H | 1M DVB/ 2.5M DMAEMA 35 NP Butanol | Woven Modacrylic | 0.050 | 4.1 | -- | -- | To Be Rerun |
| | | Woven Polyester | 0.010 | 1.2 | -- | -- | 353 |
| | | Woven Vinyl | 0.011 | 2.6 | -- | -- | 251 |
| | | Glass/ Polyester | 0.013 | 2.2 | -- | -- | 235 |
| W285-77I | 1M DVB/ 2M DMAEMA 35 NP Butanol | Woven Modacrylic | 0.052 | 4.4 | -- | -- | 57.7 |
| | | Woven Polyester | 0.010 | 1.35 | -- | -- | 4.13 |
| | | (met utility load levelling requirements under old target of 1.5 Ω -cm ² 5 μ g/cm ² /hr/M/L) | | | | | |
| | Presoak Fabrics | Woven Vinyl | 0.011 | 1.2 | -- | -- | 161 |
| 285-88 | DVB/DMAEMA 1M/5M | Woven Modacrylic | 0.048 | 3.9 | -- | -- | 76.8 |
| | 35 NP | Fine Woven Polyester | 0.012 | 1.6 | -- | -- | -- |

TABLE XI (B)

| | | | | | | | |
|--------|-----------------------|-------------------------------|-----------------|------|----|----|------------------|
| | | Fine Woven Vinyl | 0.012 | 2.3 | -- | -- | 129 |
| 285-92 | DVB/DMAEMA 1M/7.5M | Woven Modacrylic | 0.048 | 2.6 | -- | -- | 112 |
| | 35 NP | Fine Woven Polyester | 0.010 | 0.74 | -- | -- | 2,534 (LEAKS) |
| | | Fine Woven Vinyl | 0.010 | 1.9 | -- | -- | 227 |
| 285-88 | 1M/10M | Woven Modacrylic | SPALLED IN ACID | | | | |
| | 35 NP | Fine Woven Polyester | " | " | " | | |
| | | Fine Woven Vinyl | " | " | " | | |
| 285-92 | 1M/10M | Woven Modacrylic | " | " | " | | |
| | 50 NP | Fine Woven Polyester | " | " | " | | |
| | | Fine Woven Polyvinyl-chloride | " | " | " | | |
| | | Fine Woven Polyvinyl-chloride | " | " | " | | |
| 285-93 | 1M/7.5M 50NP | Woven Modacrylic | 0.043 | 2.7 | -- | -- | 322 |
| | | Fine Woven Modacrylic | 0.035 | 2.2 | -- | -- | 405 |
| | | Fine Woven Polyester | 0.010 | 0.86 | -- | -- | 933 |
| | | Fine Woven Vinyl | 0.010 | 1.4 | -- | -- | 631 |

TABLE XII
MEMBRANE SCREENING
CD1L ANION TYPES

| <u>Designation</u> | <u>Type</u> | <u>Backing Fabric</u> | <u>Leaks</u> | <u>(t,cm)</u> | <u>R = Ω-cm²</u> | <u>% Water</u> | Ion Exchange Capacity | Selectivity '1M FeCl ₃ -1N HCl |
|--------------------|---------------|---------------------------|--------------|---------------|---|--------------------|--------------------------|---|
| | | | | | | | <u>meq/gdr</u> | <u>μg Fe/hr/cm²/mol/l</u> |
| W285-66 | CD1L 30 NP | Woven Modacrylic | OK | 0.043 | 3.7 | 33.5% | 4.09 | -- |
| | 0.25 Cat | Polyester CF(9) | OK | 0.024 | 3.9 | -- | -- | 38.0 |
| | | Polyester CF(6) | OK | 0.020 | 2.6 | -- | -- | 39.7 |
| | | Polyester CH(10) | OK | 0.029 | 2.1 | -- | -- | 82.2 |
| | | Glass CH(5) | OK | 0.037 | 2.5 | -- | -- | 53.1 |
| | | Glass PE CH(4) | OK | 0.011 | 2.1 | -- | -- | 82.8 |
| W285-68 | CD1L 35 NP | Woven Modacrylic | OK | 0.042 | 3.7 | 37.1 | 4.28 | 45.7 |
| | 0.25 Cat | Non-Woven Modacrylic | OK | 0.030 | 2.6 | -- | -- | 98.4 |
| | | Polyester CF(9) | OK | 0.023 | 4.4 | -- | -- | 46.3 |
| | | Polyester CH(10) | OK | 0.028 | 2.1 | -- | -- | 128 |
| | | Glass CH(5) | OK | 0.017 | 1.5 | -- | -- | 231 (Broke on Removal) |

TABLE XII (A)

| | | | | | | | | |
|---------|---|----------------------------|----|-------|------|----|----|--------------------------------------|
| | | Woven Polyester | OK | 0.010 | 1.1 | -- | -- | 217 |
| | | Woven Polyester Presoaked | OK | 0.010 | 1.1 | -- | -- | 273 (Pre-soaked in DMAEMA & alcohol) |
| W285-72 | CD1L 27.5 NP Low Cat. | Non-Woven Modacrylic Run A | OK | 0.025 | 2.4 | -- | -- | 62 |
| | | Non-Woven Modacrylic Run B | OK | 0.031 | 2.4 | -- | -- | 49.7 |
| W285-82 | CD1L 35 NP with a 3 day presoak in DMAEMA | Woven Modacrylic | OK | 0.030 | 3.8 | -- | -- | 35.2 |
| | | Woven Polyester | OK | 0.010 | 1.48 | | | 145 |
| | | Woven V-7100 | OK | 0.011 | 2.46 | | | 63.2 |

increases in the strong ion exchange capacity of the system. While these membranes produced some membranes of normal character none was outstanding in all aspects.

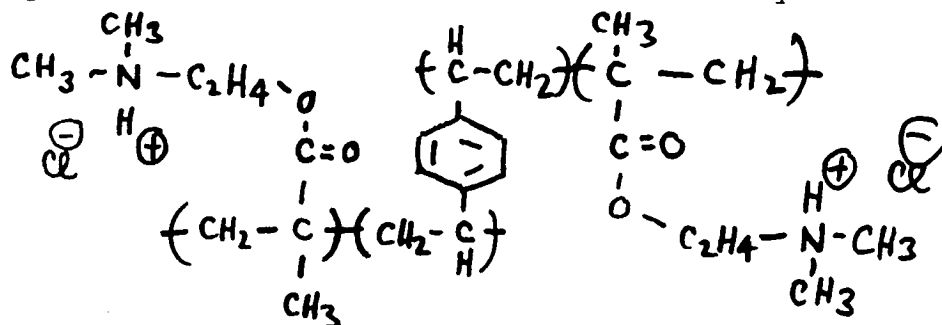
Of the reactants tested the most active were low molecular weight polyamines, such as tetraethylenepentamine.

Typical results are given in Tables VIII, IX and X. While the best resistivities are on the same order as the CD1L anion the higher NP content had an adverse effect on the selectivity of the membrane.

There was no improvement, in any composite preparation, over the standard CD1L-AA5 anion exchange membrane.

II.2.E. POLYMER VARIATIONS

The fabrication of lower cost membranes with high purity divinylbenzene and DMAEMA was explored. This divinylbenzene has become available at 75 to 80% active material and permits the fabrication of membrane systems having an ion exchange capacity of about 4.0 without the use of costly VBC.



Several formulations were made up, however, the appearance of the membranes was poor. They exhibited an apparent incompatibility with the N.P. solvent used (Ethyl benzene). This incompatibility resulted in white opaque membranes with pinhole problems. A change to butanol was made and produced consistently better membranes.

As such membranes should be inexpensive and efficient a series of membranes was made up using DVB/DMAEMA using isobutanol as the NP reagent. These membranes had varying NP contents (.35-.50 NP) and catalysts that cured at low and high temperatures. The series was made by increasing the DMAEMA to DVB ratio in steps, from 2 moles/1 mole to 10 moles/1 mole.

At the highest ratio of DMAEMA to DVB (1/10), spalling occurred in acid bath at .35 and .50 NP. Formulations at 7.5M DMAEMA per 1M of DVB produced non-spalling membranes with relatively low resistance, dropping from 4.5-5.5 $\Omega\text{-cm}^2$

2M DMAEMA/1M DVB to 2.6 to 2.7 $\Omega\text{-cm}^2$ at the 7.5 M/DMAEMA/1M DVB ratio. Selectivity loss was appreciable, dropping from 76 $\mu\text{g Fe}$ to 322 $\mu\text{g Fe/hr/cm}^2\text{/M/L}$.

These formulations were evaluated on several of the more promising fabrics. Usually the lowest resistances were found on the thinnest fabrics, a very fine woven polyester or a very fine woven polyvinylchloride. Adhesion to these fabrics in general was not outstanding. The best adhesion was found on woven modacrylic fabrics.

As these membranes were above the target resistance of 1.0 $\Omega\text{-cm}^2$ scaled-up sizes or quantities were not made up. It must be pointed out, however, that W285-71I (Table XI) 1M DVB/2 M DMAEMA, 35 NP in Butanol on 4 mil woven polyester actually met the older criteria for utility load levelling for separate electrolytes (i.e., $R = < 1.5 \Omega\text{-cm}^2$; $D = < 5 \mu\text{g Fe}^{+3}/\text{cm}^2/\text{hr/M/L}$).

II.2.F LOW RESISTANCE FABRICS

A series of non-woven and woven fabrics, a variety of catalysts, and several NP contents were used to make a number of CD1L type anion membrane variations.

Most of these backings produced membranes with lower resistance than the woven modacrylic reference fabric. (See Table XII.) Slightly more than half of the values were below $2.5 \Omega\text{-cm}^2$ in 0.1N HCl, however only four were $1.5 \Omega\text{-cm}^2$ or below and none below $1.0 \Omega\text{-cm}^2$.

Strips of membranes with various fabric backings were aged in 1 Molar FeCl_3 acidified to 1 Normal with HCl at 65°C . The results of this exposure are outlined in Table XIII.

From the tests run on thin fabrics, both woven and non-woven, we may summarize as follows:

1. woven modacrylic fabrics make excellent backings, but are usually thick and of high resistance.

TABLE XIII

Life Test

Anion Membranes

Test Solution1 Molar FeCl_3 in 1N HCl

| CODE | RESIN TYPE | FABRIC TYPE | GENERAL APPEARANCE | 45 Days* | | |
|--------------------|-----------------------------|-------------------------------|-----------------------|-----------|--|----------------------|
| | | | | t (cm) | RESISTANCE ($\Omega\text{-cm}^2$) | PHYSICAL STRENGTH |
| CD1L AA5-LC | Standard | Woven Modacrylic | OK | 0.040 | 3.9 | GOOD |
| 285-34 | CD1L with Low Temp. Cat. | Non-Woven Modacrylic/Vinyl | OK | 0.036 | 2.1 | GOOD |
| 285-40 | STD | Non-Woven Polyethylene | OK | 0.035 | 2.7 | GOOD |
| 285-42 | STD | Knit Polyester | Curled OK | 0.036 | 3.9 | GOOD |
| 285-47 | 30NP REG | Woven Aramid | OK | 0.025 | 2.3 | VERY WEAK |
| 285-52 B | DVB/DMA EMA | Woven Modacrylic | OK | 0.047 | 7.4 | |
| 285-52 C | DVB/DMA EMA | Woven Modacrylic | OK | 0.047 | 7.0 | GOOD |
| 193-606 | STD | Woven Dacron | OK | 0.012 | 1.2 | GOOD |
| 193-50 | STD | Woven Polypropylene | OK | 0.031 | 3.1 | GOOD |
| Macro Reticular | 70NP | Woven Modacrylic | OK | 0.059 | 3.1 | GOOD |

* 1080 hrs.

2. non-woven acrylic fabrics are good backings but the thinnest found to yield leak-free membranes had resistances greater than $1.0 \Omega\text{-cm}^2$.
3. non-woven glass fabrics were available in very low thickness however they would not withstand the cells acidic solution.
4. non-woven polyethylene fabrics were somewhat thick and gave good membranes except for minor blisters and high resistance.
5. non-woven polypropylene fabrics gave good saturation but resistance of leak-free membranes was above $1.0 \Omega\text{-cm}^2$.
6. woven aramid fabrics gave reasonable membranes when epoxy sized, however, generally they were dense and had high resistance. Additionally, their acid resistance was the poorest of all tested.
7. woven polypropylene fabrics gave good membranes but fabrics were either thick, or dense, yielding high-resistance products.
8. thin woven vinyl fabrics were generally dense and often shrank during cure, giving higher resistance than desired.

9. thin woven polyester fabrics were generally difficult to wet and tended to give high percentages of leaky membranes. Resistances were low but usually above the 1 Ω -cm² target

In this extensive evaluation of thin fabrics none were found that readily made leak-free membranes having low permeability and resistance of less than 1.0 Ω -cm².

Summary and Conclusions (Part II)

During the course of this contract emphasis was shifted from the generally smaller storage cell/battery units to high capacity load levelling units. The optimization of this latter activity demanded a membrane with substantially lowered resistance. Fortunately, this area of application was found to permit much higher membrane permeability. Exploratory work at NASA-Lewis indicated that these criteria were compatible with the use of cation polymeric membranes with their inherently lower resistance. As the suitability of cation membranes for this application became confirmed more and more emphasis was put on their development.

Under the initial phase of the contract, studies were carried out aimed at developing membranes with lower resistance and improved ion selectivity. These studies included considerable work on composite membranes. Composite macro-reticular membranes were made with a variety of reactive sites which were post reacted to attach desirable ion exchange groups.

Other anion studies were made using a variety of new polymeric configurations. These included the use of dichloroethylene and divinylbenzene along with some of the more usual monomers.

A variety of fabrics, both woven and non-woven, were evaluated as backing for a number of the standard and experimental ion exchange membranes. Several of these showed promise for lower resistance membranes.

Under the cation phase of the study a number of cation polymeric membranes were prepared. Most of these were prepared on several fabrics. Some were produced without any backing.

Summary and Conclusions

Conclusions

1. The development work on the composite membrane yielded active ion exchange membranes, however their properties generally were not as desirable as the regular CDLL type.
2. Polymer variations yielded some interesting membranes, some with better specific properties, but none with an outstanding combination of low resistance, target selectivity and spalling resistance.
3. Low resistance fabrics were explored in both the woven and non-woven areas. Meaningful reductions in resistance were achieved in some cases without undue loss in selectivity. While the reductions in R values were substantial,

membranes with the best overall properties still had resistances above the target of $1 \Omega\text{-cm}^2$. Several membranes of this type were evaluated for performance by the NASA REDOX Group.

4. Backed cation membranes, made on thinner woven and non-woven fabrics, had lowered resistance values. Fabricating these membranes, at low thickness, was a difficult and exacting task and would probably require special production techniques. Several membranes of this type were evaluated for performance by the NASA REDOX Group.

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| 16. Two new polymeric ion exchange membranes have been synthesized for the purpose of fulfilling the needs of both resistivity and anolyte/catholyte separation for competitive utility load levelling utilizing the new DOE/NASA mixed electrolyte "REDOX" battery. One candidate, an anion exchange membrane designated "VCTP" has a measurable resistivity, in 0.1N HCl, of < 1.0 ohm-cm ² , ferric ion diffusivity and under 1500 µg Fe/cm ² /Hr/M/L. Another candidate, a cation exchange membrane designated "CPS" has a measurable resistivity in 0.1N HCl of < 1.0 ohm-cm ² with ferric ion diffusivity under 1000 µg Fe/cm ² /Hr/M/L. Both candidates thus meet mixed electrolyte utility load levelling criteria. Several modifications of the older "CDIL" anion exchange membrane failed to meet utility load levelling "REDOX" battery criteria using the <u>un</u> -mixed electrolyte REDOX cell. | | | |
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