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# ANION PERMSELECTIVE MEMBRANE

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# July 17, 1984

Prepared for NATIONAL AERONAUTICS AND SPACE ADMINISTRATION Lewis Research Center Cleveland, Ohio 44135 Under Contract DEN 3-264

for

# U.S. DEPARTMENT OF ENERGY Office of Advanced Conservation Technologies Division of Energy Storage Systems Washington, D.C. 20545

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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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MS 309-1

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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NASA Classification Page (faces rear)

#### 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 conductivehighly 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-cm<sup>2</sup> and its ferric ion permeability must not exceed 5 micrograms of iron per cm<sup>2</sup> per hour in a one formal solution concentration variance of ferric chloride at pH = 0.

Part B: The development and testing of highly conductivemoderately 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 cf 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-cm<sup>2</sup> 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 pH = 0.

- <u>Part A</u>: Despite several testings of new chemistries to yield superconductive tight polyamine membranes of the CDLL 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 CDLL membrane type but none yielded the required low resistance-low iron permeability required for utility load levelling.
- b) The synthesis of the CDLL 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 (1000% 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 highconductance coupled with low iron permeability that we

needed for utility load levelling.

 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 <u>not</u> 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<sup>2</sup> 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-cm<sup>2</sup> in 0.1N HCl.
- 2. Permeability ranges from 50 to 7700  $\mu$ gFe<sup>+3</sup>/cm<sup>2</sup>/hr/M/L with higher permeability numbers being capable of running at high current densities.
- 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.
- 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 gualifications:

- 1. Resistivity < 1.0 ohm-cm<sup>2</sup> in 0.1N HCl.
- 2. Permeability ranges from 4150 to 11700  $\mu gFe^{+3}/cm^{2}/hr/M/L.$
- Membranes capable of being prepared and supplied in the 3 to 7 mil thickness range without fabric backing.
- 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  $\Omega$ -cm<sup>2</sup> in 0.1N HCl.
- Membrane porosity as measured by  $Fe^{+3}$  diffusion not established but estimated in range of  $10^3$  to  $10^4$ µgFe/cm<sup>2</sup>/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 pinholefree films up to 1.5 ft<sup>2</sup> 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 meg per dry gram resin and water contents of 34 to 67.5% (Wet Basis). The electrical resistivities (Rp) in 0.1N HCl at room temperature were all less than 1.0  $\Omega$ -cm<sup>2</sup> and the film porosities as measured by diffusion of Fe<sup>+3</sup> were 50 to 7700 µgFe/cm<sup>2</sup>/hr/M/L (Table I). TABLE I

# PROPERTIES OF CPS UNBACKED CATION MEMBRANES

_1D	GAUGE (MILS)	RESISTIVITY IN 0.1N HCL (онм-см <sup>2</sup> )	H <sub>2</sub> O CONTENT	IEC (meq/dgr)	INTERSTITIAL MOLALITY (M/L)	DIFFUSION_RATE (44gFe/_cm <sup>2</sup> _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/cm<sup>2</sup> 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  $\mu$ gFe/cm<sup>2</sup>/hr/M/L. The electrical resistivity in 0.1N HCl for all samples was less than 1  $\Omega$ -cm<sup>2</sup> at ambient temperature.

Post treatment of the VCTP membrane at elevated temperature in FeCl<sub>3</sub> solution resulted in a substantial decrease of film porosity with only a small increase in resistivity (Table III). Immersion of a membrane in 1MFeCl<sub>3</sub>, 3NHCl solution at 65°C for 64 hrs. reduced the Fe diffusion from 4150 to a stable level of 1390  $\mu$ gFe/cm<sup>2</sup>/hr/M/L and showed a very small rise in Rc of 0.5 to 0.64  $\Omega$ -cm<sup>2</sup> (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)	H20 CONTENT (%)	RESISTIVITY <sup>1</sup>	Fe DIFFUSION <sup>2</sup> D <sub>FE2</sub> (ucFe/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	FRANGIBL	E, TEARS E	ASILY	

1 Resistivity measured with contact probes in 0.1NHCL.

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<sup>2</sup>Fe Diffusion solutions, lMFeCl<sub>3</sub>, 0.5NHCl vs. 2MCaCl<sub>2</sub>, 0.5NHCl.

#### TABLE III

PROPERTIES OF VCTP UNBACKED MEMBRANES -POST TREATED IN FECL3 3N HCL SOLUTION

TEMP. 65 C

SAMPLE NO.	TIME IN SOLUTION (HR)	Fe DIFFUSION GFe/cm <sup>2</sup> HRM/L)	RESISTIVITY <sup>1</sup> R ( <b>r</b> _cm <sup>2</sup> )
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	

Resistivity measured with contact probes in C.INHCL. <sup>2</sup> Fe Diffusion solutions, IMFeCl<sub>3</sub>, 0.5NHCl vs. 2MCaCl<sub>2</sub>, 0.5NHCl.





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

FILM NO.	REACTION TIME (HRS.)	RESISTIVITY,R <sub>e</sub> IN 0.1NHCl (Ω-CM <sup>2</sup> )	Fe DIFFUSION DFe µgFe/CM <sup>2</sup> /HR/M/L
253	2	0.91	5477
	3	0.81	<b>9</b> 113
	4	0.71	
	6	0.64	
254	2	0.84	8341
	3	0.79	<b>9</b> 565
	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<sup>-</sup> 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. <u>MEMBRANE SEPARATORS FOR THE DOE/NASA</u> 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  $\Omega$ -cm<sup>2</sup>), much lower than the W285-57, a comparable medium capacity (IEC 2.34) anion exchange membrane (4.9  $\Omega$ -cm<sup>2</sup>). The cation membrane also has better iron selectivity.

Several cation exchange membranes were found having resistances below one (1.0)  $\Omega$ -cm<sup>2</sup> 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

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#### MEMBRANE SCREENING CATION AND ANION TYPES

		Backing	0.1N HC1 Resistance			Ion Exchange Capacity	Selecțivity 1M FeCl <sub>3</sub> -1N HCl
Designation	Туре	Fabric	<u>(t,cm)</u>	$\underline{\mathbf{R} = \Omega - \mathbf{cm}^2}$	* Water	meq/gdr	µg Fe/hr/cm <sup>2</sup> /mol/l
W 285-56	Cation	Woven Modacrylic	0.055	2.1	39.0	2.20	151 (201*)
₩ 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			(30 NP)	2.3***	116
		Polyester**					
	Cation	Non-Woven Glass**			(30 NP)	2.3***	107
Typical Control	CD1L Anion	Woven Modacrylic	0.040	4.3	33.7	4.22	35

\* 0.5 N HCl, 1M FeCl<sub>3</sub>/0.5 N HCl
\*\* Incomplete saturation
\*\*\* Typical value

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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 posttreatment 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 posttreatment. 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

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#### MEMBRANE SCREENING CATION TYPES

	Backing	Look			٩	Ion Exchange Capacity	Selectivity lM FeCl <sub>3</sub> -lN HCl
Designation	Fabric	Test	(t,cm)	$\underline{\mathbf{R}} = \Omega - \mathbf{c}\mathbf{m}^2$	<u>Water</u>	meq/gdr	µg Fe/hr/cm <sup>2</sup> /mol/l
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	ОК	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

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#### MEMBRANE SCREENING CATION TYPES

							Ion Exchange Capacity	Selectivity lM FeCl <sub>3</sub> -lN HCl
Designation	Туре	Backing Fabric	Leaks	(t,cm)	$\underline{R} = \Omega - cm^2$	Water	meq/gdr	µg Fe/hr/cm <sup>2</sup> /mol/l
285-87 A (V195-83)	High NP	Woven Modacrylic	ОК	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	ОК	0.045	1.84	35	2.28	89.5
285-89 (V195-xx)	MOD NP	Non-Woven Modacrylic	ОК	0.032	0.90			97.4
285-94	Very High NP (50)	Woven Modacrylic	ОК	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	ОК	0.044	1.2	هن ب		199
		Non-Woven Modacrylic	OK slight blister	0.024 s	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

Treatment	Thickness	Resistivity <u>0.01N NaCl</u>	Resistivity 0.1N HC1
	(cm)	$(\Omega - cm^2)$	$(\Omega - cm^2)$
Control No treatment	0.055	95.9	4.1
Meta-DCX (High purity)	0.55	21.7	9.2
75/80%m-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

 $\alpha \quad \alpha' - Dichloro-p-xylene$ 

#### TABLE IX

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

Treatment	<u>Thickness</u> (cm)	Resistivity <u>0.01N NaCl</u> (Ω-cm <sup>2</sup> )	Resistivity <u>0.lN HCl</u> (Ω-cm <sup>2</sup> )
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

Treatment	<u>Thickness</u> (cm)	Resistivity <u>in 0.01N NaCl</u> (Ω-cm <sup>2</sup> )	<u>Thickness</u> (cm)	Resistivity <u>in 0.lN HCl</u> (Ω-cm <sup>2</sup> )
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

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### TABLE XI

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#### MEMBRANE SCREENING NON-VBC ANION TYPES

Designation	Туре	Backing Fabric	(t,cm)	$\underline{R} = \Omega - cm^2$	% Water	Ion Exchange Capacity meg/gdr	Selectivity 1M FeCl <sub>3</sub> -1N HCl <u>µg Fe/hr/cm<sup>2</sup>/mol/1</u>
W285-74A	1M DVB/ 2M DMAEMA	Woven Modacrylic	0.059	4.1			
	10 11	Woven Polyester	0.011	Leaks			
		Woven Vinyl	0.021	9.7			
W285-74C	1M DVB/2.5M DMAEMA	Woven Modacrylic	0.062	3.9			
	40 NP	Woven Polyester	0.010	Leaks			
		Woven Vinyl	0.021	9.0			
W285-76D	1M DVB/ 2M DMAEMA 35 ND	Woven Modacrylic	0.045	3.8			
	Early Cat.	Woven Polyester	0.012	1.8			
		Woven Vinyl	0.018	8.4			
W285-76E	1M DVB/ 2M DMAEMA 35NP	Woven Modacrylic	0.044	2.9			
	Late Cat.	Woven Polyester	Massi Leaki	ve			

	9.	ı	TABLE XI	(A)		•	n de la constante de la const
W285-77F	1M DVB/ 2M DMAEMA 35ND	Woven Modacrylic	0.054	5.4	34.4	3.27	133
	Presoak	Woven Polyester	0.010	2.3			465
		Woven Vinyl	0.018	4.0			
W285-77G	1M DVB/ 2M DMAEMA 35 NB	Woven Modacrylic	0.049	4.8	33.0	3.30	• 76.2
	Butanol	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	Woven Modacrylic	0.050	4.1			To Be Rerun
	Butanol	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 NB	Woven Modacrylic	0.052	4.4			57.7
	Butanol	Woven Polyester ( of 1.5 Ω-cm	0.010 met utili <sup>2</sup> 5 µg/cm	<u>1.35</u> ty load 1 <sup>2</sup> /hr/M/L)	 evelling rea	 quirements ur	der old target
	Presoak Fabrics	Woven Vinyl	0.011	1.2			161
285-88	DVB/DMAEMA 1M/5M	Woven Modacrylıc	0.048	3.9			76.8
	35 NP	Fine Woven Polvester	0.012	1.6			

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		1	TABLE XI	(B)	,	د
		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	**	90 99		
		Fine Woven Vinyl	"	II II		
285-92	1M/10M	Woven Modacrylic	**	11 II		
	50 NP	Fine Woven Polyester	"	en ee		
		Fine Woven Polyvinyl- chloride	11			
		Fine Woven Polyvinyl- chloride	••	H H		
285-93	1 <b>m/7.</b> 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

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#### MEMBRANE SCREENING CD1L ANION TYPES

Designation	Туре	Backing Fabric	Leaks	(t.cm)	$R = \Omega - cm^2$	% Water	Ion Exchange Capacity meg/gdr	Selectivity 'IM FeCl <sub>3</sub> -IN HCl
W285-66	CD1L 30 NP	Woven Modacrylic	<u> </u>	0.043	3.7	33.5%	4.09	
	0.25 Cat	Polyester CF(9)	ОК	0.024	3.9			38.0
		Polyester CF(6)	OK	0.020	2.6			39.7
		Polyester CH(10)	ОК	0.029	2.1			82.2
		Glass CH(5)	OK	0.037	2.5			53.1
		Glass PE CH(4)	ОК	0.011	2.1			82.8
W285-68	CD1L 35 NP	Woven Modacrylic	ОК	0.042	3.7	37.1	4.28	45.7
	0.25 Cat	Non-Woven Modacrylic	ОК	0.030	2.6			98.4
		Polyester CF(9)	ОК	0.023	4.4			46.3
		Polyester CH(10)	ОК	0.028	2.1			128
		Glass CH(5)	ОК	0.017	1.5			231 (Broke on Removal)

TABLE XII (A)

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		Woven Polyester	ОК	0.010	1.1	 	217
		Woven Polyester Presoaked	ОК	0.010	1.1	 	273 (Pre- soaked in DMAEMA & alcohol)
W285-72	CD1L 27.5 NP Low Cat.	Non-Woven Modacrylic Run A	ОК	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	Woven Modacrylic	ОК	0.030	3.8	 	35.2
	day presoak in DMAEMA	Woven Polyester	OK	0.010	1.48		145
		Woven V-7100	ОК	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 CDLL 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/l mole to 10 moles/l 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  $4.5-5.5 \ \Omega-cm^2$ 

2M DMAEMA/1M DVB to 2.6 to 2.7  $\Omega$ -cm<sup>2</sup> at the 7.5 M/DMAEMA/ 1M DVB ratio. Selectivity loss was appreciable, dropping from 76 µg Fe to 322 µg Fe/hr/cm<sup>2</sup>/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  $\Omega$ -cm<sup>2</sup> 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  $\Omega$ -cm<sup>2</sup>; D = < 5 µg Fe<sup>+3</sup>/cm<sup>2</sup>/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 CDLL 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  $\Omega$ -cm<sup>2</sup> in 0.1N HCl, however only four were 1.5  $\Omega$ -cm<sup>2</sup> or below and none below 1.0  $\Omega$ -cm<sup>2</sup>.

Strips of membranes with various fabric backings were aged in 1 Molar FeCl<sub>3</sub> acidified to 1 Normal with HCl at  $65^{\circ}$ C. The results of this exposure are outlined in Table XIII.

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

 woven modacrylic fabrics make excellent backings\_but are usually thick and of high resistance.

#### TABLE XIII

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### Life Test

### Anion Membranes

## Test Solution

# 1 Molar FeCl<sub>3</sub> in 1N HCl

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

\* 1080 hrs.

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- 2. <u>non-woven acrylic</u> fabrics are good backings but the thinnest found to yield leak-free membranes had resistances greater than 1.0  $\Omega$ -cm<sup>2</sup>.
- 3. <u>non-woven glass</u> fabrics were available in very low thickness however they would not withstand the cells acidic solution.
- 4. <u>non-woven polyethylene</u> fabrics were somewhat thick and gave good membranes except for minor blisters and high resistance.
- 5. <u>non-woven polypropylene</u> fabrics gave good saturation but resistance of leak-free membranes was above 1.0  $\Omega$ cm<sup>2</sup>.
- 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.
- 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  $1 \ \Omega-cm^2$  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  $\Omega$ -cm<sup>2</sup>.

#### 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 <u>initial</u> 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 macroreticular membranes were made with a variety of reactive sites which were post reacted to attach desireable ion exchange groups.

Other anion studies were made using a variety of new polymeric configurations. These included the use of dichloroxylene 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

- The development work on the composite membrane yielded active ion exchange membranes, however their properties generally were not as desireable as the regular CDLL type.
- 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  $\Omega$ -cm<sup>2</sup>. Several membranes of this type were evaluated for performance by the NASA REDOX Group.

4. Backed cation membranes, made on thinner woven and nonwoven 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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