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ANION PERMSELECTIVE MEMBRANE

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NOTICE

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A Summary Report
Anion Permselective Membrane
DEN 3-137

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TABLE OF CONTENTS

Tables

TABLE OF CONTENTS (Continued)

FOREWORD

This document constitutes the final report for the work accomplished between June 1979 and June 1980 by Ionics, Incorporated, for the National Aeronautics and Space Administration, Lewis Research Center, under Contract DEN 3-137 entitled SYNTHESIS AND CHARACTERIZATION OF IMPROVED ION SELECTIVE SEMIPERMEABLE ANION EXCHANGE MEMBRANES.

Dr. Russell B. Hodgdon provided overall program management. The principal investigator was Warren A. Waite with major contributions from R. B. Hodgdon, A. Scieszko, and C. H. Swenson.

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ABSTRACT

The efforts on the synthesis of polymer anion redox membranes for the period covered in the report, were mainly concentrated in two areas, membrane development and membrane fabrication. The first of these areas, membrane development, covered the preparation and evaluation of experimental membrane systems with improved resistance stability and/or lower permeability.

The experimental membranes prepared and evaluated in the first area fell into several general groups or series. One such series was a number of variations made in the formulation and preparation of the prime candidate CD1L system.

These variations encompassed changes in NP quantity and type and changes in the ratio of the monomers used to make the membrane polymer. Similarly cure and catalyst studies along with the use of various new fabrics were explored - as well as blending various percentages of the number one and number two candidate polymer systems.

Another facet of the exploratory program produced membranes using other cross-linking agents and blends of cross-linking agents.

The second area of activity, membrane fabrication, covered the laboratory scale production of prime candidate membranes in quantities of up to two hundred and sizes up to 18 inches x 18 inches (46 cm x 46 cm). These small (10" x 11") and medium sized membranes were mainly for assembly into multicell units. Improvements in

processing procedures and techniques for preparing such membrane sets have lifted yields to over 90%.

The formulations chosen for application in this phase of the program, were of the CD1L type. The scaled up candidates were in the 0.25 to 0.275 NP range. The latest prime candidate membrane system has an NP of .275 and is made with a greatly reduced catalyst level. Preliminary results indicate such membranes give substantially improved performance in multicell stacks. Such membranes have been used by NASA-Lewis to make four 40 cell pair stacks which have a one to three kilowatt capacity.

1.0 Introduction and Summary

Contract DEN 3-137, Development and Preparation of Redox Cell Anion Exchange Membranes represents a continuation of the efforts to synthesize, develop and evaluate anion permselective membranes to be used as cell separators in the redox energy storage system under development at the NASA-Lewis Research Center. Under previous contracts a number of candidate membranes of widely different chemical properties had been synthesized (DEN 3-1 and NAS 3-20108).

These membranes had been evaluated and produced on a limited scale for further testing. Several of the most promising of these had been formulated with coarse adjustments of NP, monomer ratios and processing to yield anion membranes of good redox cell efficiencies. Under this contract the most promising of these membrane systems was selected (CD1L) and minor adjustments in its composition evaluated. Simultaneously with this optimization phase, new membrane systems were explored using other monomers, other cross-linking agents, other NP contents and other fabrics.

The processing of the CD1L membrane system was optimized and substantial improvements in the ease of processing, the yield and the ability to produce larger size membranes was developed. Sizes up to 18" x 18" and quantities of up to 200 membranes of a particular type have been produced in good yield using these new-techniques.

The membranes produced, after characterization were shipped to the NASA-Lewis Research Center for individual evaluation and/or utilization in Redox battery cells.

2.0 Summary of Results

A series of optimization studies were made under contract to improve the CD1L membranes performance. The results of these studies are listed below:

- CP4L/CD1L blends were found to foul and increase in resistance at a high rate.
- Small variations (5 or 10%) in VBC or DMAEMA content did not alter the CD1L membrane systems performance markedly.
- Raising the NP content to 0.275 produced a membrane with improved resistivity and resistance stability without substantially increasing the permeability.
- Reduced catalyst concentrations produced membranes with better electrical performance in multicell redox battery stacks.
- Improved processing techniques were developed which achieved yields of over 95% for this type of membrane. These techniques were used to produce sizes up to 18" x 18" and certain 10" x 11" membranes in quantities of two hundred each.

Incorporating these changes the prime candidate membrane system currently is a CD1L type formulation with 0.275 NP and 0.0625% catalyst. The performance of this membrane in multicell redox battery stacks was reported to be approximately twenty percent better than earlier formulations in terms of efficiency.

The use of another series of cross-linking monomers to replace VBC was explored. The most promising of this series, a trifunctional acrylate, gave some membranes whose preliminary properties appear to approximate those of the CD1L types.

3.0 Preparation of Candidate Membranes

Early in the contract period the prime candidate membrane was the CD1L-A5. This VBC-DMAEMA copolymer was produced in some quantities. During the course of the contracts research and development activities an optimized variation was generated.

This new prime candidate membrane in the latter part of the contract was modified by adopting a drastically lowered catalyst concentration (from 0.5% to 0.0625%) and an increased NP content (0.25 to 0.275). A variety of tests in various redox cells at NASA-Lewis indicated these changes gave a better balance of properties and under dynamic conditions substantially improved performance.

In the course of these studies, at various times it became necessary to uniformly and reliably produce reasonably large quantities of candidate membranes in the laboratory environment. A large percentage of the contract's effort was spent on the fabrication of such membranes and problems associated with their processing, characterization and evaluation. A discussion of some of these parameters and activities follows.

3.1 CD1L Membrane Formulations and Procedures

The current NASA-Lewis redox battery system employs one type of anion membrane to separate the iron and chromium electrolytes - the CD1L. This CD1L type is by far the most important membrane and the only one that has been prepared in substantial quantities. At the start of this contract this ionic VBC-DMAEMA copolymer was prepared with a 0.25NP and a catalyst level of 0.5%. During the course of the contract the membrane has been improved and the most recent prime candidate has an NP content of 0.275, a catalyst level of 0.0625% and a final thickness of about 0.040 cm. This membrane is also used in the state-of-charge monitoring cell.

The membrane NASA-Lewis has selected for the rebalance cell is the earlier CD1L-A5 formulation (0.25NP-0.5% Cat.). When prepared on the standard modacrylic fabric this gave a very tight, highly selective membrane 0.060 cm thick.

The third membrane variation was another CD1L type. This formulation had an NP content of 0.40 and used 0.5% catalyst. Both the prime candidate membrane and the 0.25NP-0.5% catalyst membrane can be made using identical techniques, equipment and materials. It is not anticipated that their fabrication will require any appreciable separate development efforts.

The techniques for fabrication of the CD1L-AA5 anion membrane have been standardized and while rather complex they are direct and dependable. The steps are outlined below:

1. Cool all ingredients before starting.
2. Add the NP (IBUOH) and DMAEMA.
3. Add the VBC (Hold at 5 to 10°C).
4. Add the catalyst, Vazo 64.
5. Degas for about 15 min. at 50 to 100 mm.
6. Load into trays and lay up promptly.
7. Cure overnight.
8. Cool and remove membranes.

A number of procedural parameters have been explored separately and in the course of the fabrication of various batches of membranes. These have included the introduction of normal contaminants (silicone oil, water, etc.), variations in cure temperature, fabric lot, catalyst concentration, monomer content and batch size. All of the resultant membranes have been fully characterized (ion exchange capacity, resistivity, water content) and checked in screening tests for permeability and stability. Any deviations of properties was extremely minor and well within acceptable tolerance limits.

3.2 Sizes, Quantities and Characterization of CD1L Type Membranes

The fabrication of test and prototype redox battery units by NASA-Lewis under this and associated contracts, on two occassions required quantities of about 200 membranes in 10.5" x 11.5" (27 cm x 29 cm) sizes.

A number of smaller runs of 10.5" x 11.5" membranes were also produced as well as batches of 10 to 15 membranes in sizes up to 18" x 18" (46 cm x 46 cm). All these sizes and quantities were processed in the laboratory with reasonable convenience.

Batch sizes were scaled up to the six liter range during the contract. This permits small lots of the 18" x 18" membranes and reasonable batches of 10.5" x 11.5" anion membranes to be made at one time.

All batches of membranes made for any phase of the program were characterized for quality control data base accumulation. This characterization included ion exchange content (total, strong, and weak), electrical resistance and water content. The results of the two largest runs on CD1L-A5 and CD1L-AA5 are deliniated in Tables 3.2-I and 3.2-II, for reference.

TABLE 3.2-I

TWO HUNDRED MEMBRANE SHIPMENT

CD1L-AA5 STD. CAT.

Lot No. - DH	1	2	3	4	5	6
Catalyst (%)	0.5	0.5	0.5	0.5	0.5	0.5
NP	0.275	0.275	0.275	0.275	0.275	0.275
Water Content (%)	37.2	37.5	37.0	38.6	37.7	36.4
Electrical Resistance 0.1N HCl (Ω-cm^2)	4.2	4.4	4.0	4.8	4.8	4.8
Thickness (cm)	-	-	-	-	-	-
I.E.C. (meq/dgr)						
Total	4.38	4.24	4.28	4.37	4.25	4.40
Strong	1.90	1.84	2.20	2.15	2.20	2.04
Weak	2.48	2.40	2.08	2.22	2.05	2.36

TABLE 3.2-II

TWO HUNDRED MEMBRANE SHIPMENT

CD1L-AA5 - LOW CAT.

W233, Lot No.-DH	21A	24B	22C	22D	23E	24F	25G	26II
Catalyst (%)	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625	0.0625
NP	0.275	0.275	0.275	0.275	0.275	0.275	0.275	0.275
Water Content (%)	41.0	41.0	42.1	41.0	40.3	41.4	39.1	39.8
Electrical Resistance 0.1N HCl (Ω-cm^2)	4.3	4.1	4.1	4.2	3.9	3.9	3.6	4.0
Thickness (cm)	0.040	0.036	0.036	0.037	0.036	0.038	0.039	0.035
I.E.C. (meq/dgr)								
Total	4.22	4.67	4.37	4.30	4.85	4.51	4.78	4.84
Strong	2.07	2.03	2.04	2.04	2.20	2.00	2.23	2.21
Weak	2.15	2.65	2.28	2.26	2.65	2.51	2.57	2.63

4.0 Monomer Variations

As the CD1L anion membrane system became the prime candidate it was considered necessary to explore the effects of minor variations of the amounts of the two comonomers on the properties of the finished membranes. Not only could such a study yield a membrane with improved performance but it would define the sensitivity of the system for factory weighing and measuring procedures in the future.

To achieve these objectives individual sets of membranes with 5, 10 and 20 mole percent excess of VBC and DMAEMA were prepared. The resultant membranes were characterized and evaluated in redox cells.

Another modification of the CD1L system was the replacement of varying percentages of DMAEMA with diethylaminoethylmethacrylate (DEAEMA). This material was tried as the amine monomer replacement as it was much slower to form adducts with the VBC than the regular DMAEMA due to the larger ethyl groups attached to the 3° amine function during quaternization.

The final monomer modification tried was the blending of the CD1L formulation with the CP4L formulation. It was hoped that such blends might combine the superior electrical resistances of the CD1L series with the superior chemical resistance of the CP4L series.

4.1 Membrane System with Increased VBC

While major variations (± 25%) in the VBC content of the CD1L formulation have not resulted in improved membranes, it was felt that improvements might be achieved by minor adjustment of the VBC content.

To verify this, formulations with an increase of 5, 10 and 20 mole percent in the VBC content of the prime candidate system were made into membranes. The DMAEMA content of these membranes was kept constant and the NP adjusted to maintain it at 0.25.

These membranes were prepared in the usual manner. Their modulus appeared slightly higher than usual and increased with increasing VBC content. Increasing the VBC reduced the time available for laying up membranes somewhat as it tended to accelerate the adduct formation reaction between the VBC and DMAEMA and thus the viscosity.

The membranes produced were characterized for ion exchange capacity, water content and resistance in 0.1N HCl. The results of these tests indicated that the increased VBC content tended to increase the initial resistance of the membranes very slightly - and decrease their total ion exchange capacity somewhat.

While sample membranes were sent to NASA-Lewis for more definitive static and dynamic tests in their various test cells, at Ionics a limited iron fouling test was run in 2M $FeCl_3$ acidified with 2N HCl. The results of this 300+ hour test indicated (as did similar but not identical tests at NASA-Lewis) that increased VBC tended to increase iron fouling. The results of these tests along with the values from the characterization of these membranes and NASA-Lewis iron permeability tests are included in Table 4.1-I and 4.1-II. Generally significant reduction in permeability to iron appeared to be achieved only at considerable increase in electrical resistance from iron fouling.

TABLE 4.1-I

MEMBRANE CHARACTERIZATION DATA

INCREASED VINYLBENZYLCHLORIDE

Excess VBC*	5%	10%	20%	Typical CD1L-A5
NP	0.25	0.25	0.25	0.25
Water Content	36.5%	36.4%	34.7%	35.8
Electrical Resistance in 0.1NHCl (Ω-cm^2)	4.2	4.6	4.9	4.4
Thickness (cm)	0.043	0.042	0.044	0.042
I.E.C. (meq/dgr)				
Total	4.17	4.06	4.00	4.33
Strong	2.30	2.10	2.17	2.11
Weak	1.87	1.96	1.83	2.22

*Extra mole percent of VBC over standard formulation.

TABLE 4.1-II

IRON FOULING AND PERMEABILITY TEST DATA*

INCREASED VINYL BENZYLCHLORIDE

Excess VBC	5%	10%	20%	Typical CD1L-A5
NP	0.25	0.25	0.25	0.25
Water Content	36.5%	36.4%	34.7%	-
Electrical Resistance (Ω-cm^2) Initial In 0.1NHCl	4.2	4.6	4.9	4.4
In 2M$FeCl_3$ with 2NHCl				
360 hrs.	16.3	14.4	22.4	-
Permeability* μGmFe/Hr/cm^2	15	16	9	14

*Permeability data supplied by NASA-Lewis Redox Project.

4.2 Membrane System with Increased DMAEMA

As in the case of the VBC it was decided to investigate the effects of some minor variations in the DMAEMA content of the CD1L formulation. Similarly while 1.5 and 2.5 moles of DMAEMA had been tried as well as the standard two moles with one mole of VBC, it was considered possible that the effects of a small excess over standard of 5, 10 and 20 mole percent in the DMAEMA content might improve the performance of the anion membrane system. In line with this reasoning such a series of membranes with adjusted DMAEMA were prepared.

The amount of VBC in these membranes was held constant. The NP was adjusted to maintain it at 0.25.

The batches were processed in the usual manner and displayed no obvious differences in mechanical properties or physical appearance. The resulting membranes were tested to determine their ion exchange capacity, as well as their water content and resistance in 0.1N HCl. The results of these tests are listed in Table 4.2-I.

As would be expected, increasing the DMAEMA increases the total capacity and the weak base capacity, however, the total strong base capacity appears slightly lower than usual. The decrease in electrical resistivity within the series and the slight increases in water content are in the direction one would anticipate.

The decrease in resistivity seems to be slightly greater than would be expected from the total increase in capacity. However, the slight increase in water content may have magnified this improvement.

Samples of these membranes were tested for iron fouling in the 2M $FeCl_3$/2NHCl solutions. The results of these tests after 192 and 360 hours can be found in Table 4.2-II.

The results of the fouling tests seem to be somewhat ambiguous as were similar tests run at NASA-Lewis.

In other tests at NASA-Lewis the permeability of these membranes to iron was found to be somewhat higher than the standard CD1L formulation. (Table 4.2-II)

In conjunction with each other, this DMAEMA set and the preceding VBC set of experiments have shown that minor variations in quantity of the comonomers used in the CD1L formulations will not produce dramatic variations in membrane properties. While this is in some way disappointing it does indicate that if the CD1L formulation is used in production, normal variations in measurement of quantities of the comonomers (1 to 2%) should not produce a membrane with noticeably deficient properties.

TABLE 4.2-I

MEMBRANE CHARACTERIZATION DATA

INCREASED DIMETHYLAMINOETHYLMETHACRYLATE STUDY

Excess DMAMEA*	5%	10%	20%
NP	0.25	0.25	0.25
Water Content	35.3%	36.0%	37.8%
Electrical Resistance 0.1N HCl (Ω-cm^2)	3.7	3.5	3.0
Thickness (cm)	0.041	0.041	0.043
I.E.C. (meq/dgr)			
Total	4.22	4.30	4.43
Strong	1.91	1.82	1.58
Weak	2.31	2.48	2.85

*Extra mole percent of DMAMEA over standard formulation.

TABLE 4.2-II

IRON FOULING AND PERMEABILITY DATA

INCREASED DIMETHYLAMINOETHYLMETHACRYLATE

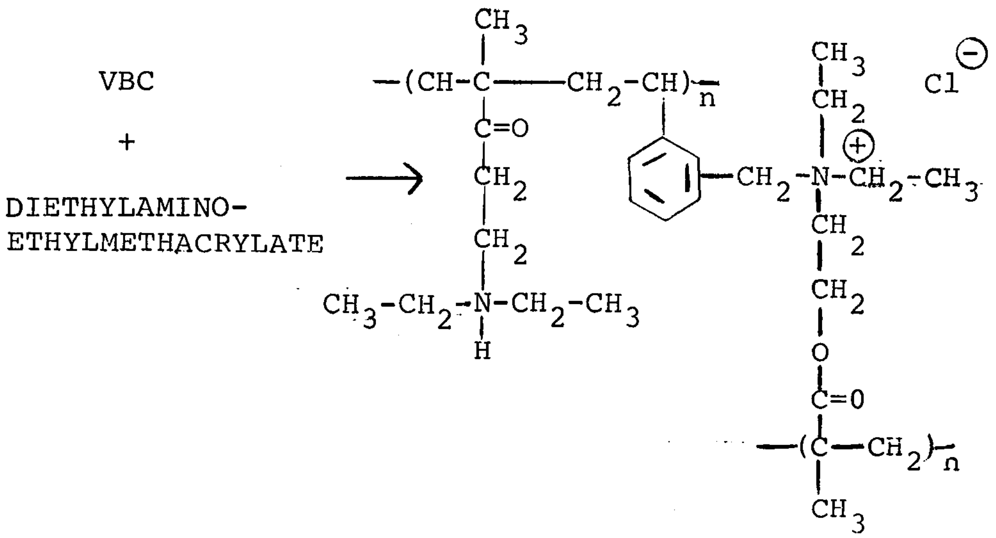
Excess DMAMEA	5%	10%	20%	CD1L-A5
NP	0.25	0.25	0.25	0.25
Water Content	35.3%	36.0%	37.8%	36.1%
Electrical Resistance (Ω-cm^2) Initial-In 0.1NHCl	3.7	3.5	3.0	4.4
In-2MFeCl$_3$ with 2NHCl				
192 hrs.	15.3	15.9	12.3	15.3
360 hrs.	14.7	15.3	13.5	16.0
Permeability* μGm Fe/Hr/cm^2	18	17	30	14

*Permeability data supplied by NASA-Lewis Redox Project.

4.3 Evaluation of Diethylaminoethylmethacrylate In Redox Membranes

An investigation was made into the use of diethylaminoethylmethacrylate as a replacement for various portions of the dimethylaminoethylmethacrylate in the CD1L-A5 formulation. This substitution was tried and as hoped it proved substantially less reactive than the "dimethyl", yet reactive enough to make a good polymer sheet.

CE1L



Using the "diethyl" for all of the dimethyl of the CD1L-A5 (0.25NP) formulation on a mole for mole basis was first explored by making some 5" x 5" membranes. After producing two reasonably satisfactory small trials a third batch was made in the 10.5" x 11.5" size. The resultant membranes were leak free, somewhat lower in modulus, and generally good in appearance.

These were analyzed to determine if the cross linking had proceeded per usual through the VBC. When this was verified, a series of experiments were run in which 25, 50, and 75 mole percent of the dimethyl was replaced with diethyl. This series was then characterized for ion exchange content, electrical resistance in 0.1N HCl and water content.

The slightly higher molecular weight of the diethylaminoethylmethacrylate reduces the theoretical ion exchange capacity of the membrane below that expected for one with 100% "methyl". The intermediate mole percentages producing intermediate ion exchange capacities.

The advantage in the use of the ethyl is that it forms the high viscosity adducts with VBC at a much slower rate. This slower rate permits greater latitude in fabrication techniques as the comonomer solution does not increase appreciably in viscosity during preparation of the membranes.

The characterization of the cured membranes may be found in Table 4.3-I.

Sample membranes from all four variations were sent to NASA-Lewis for their evaluation and comments. Meanwhile, despite the slightly higher initial resistance values, fouling tests were run in $FeCl_3$/HCl solutions.

Rather surprisingly, the ethyl formulations increased in resistance much more rapidly than the standard formulations. The results of these fouling tests paralleled those ran at NASA-Lewis in Fe/HCl solutions of somewhat different concentration.

Table 4.3-II contains some results of Ionic's iron fouling tests along with the results of NASA-Lewis test of iron permeability. While the permeability of these membranes to the Fe ions was good the rapid increase in the resistance of the membranes was judged to render them unacceptable.

TABLE 4.3-I

MEMBRANE CHARACTERIZATION DATA

Evaluation of Diethylaminoethylmethacrylate

Composition	Ethyl* 25%	Ethyl 50%	Ethyl 75%	Ethyl 100%	CD1L
NP	0.25	0.25	0.25	0.25	0.25
Water Content	34.7%	35.8%	35.9%	36.8%	35.2%
Electrical Resistance 0.1NHCl (Ω-cm^2)	5.7	4.9	5.2	4.9	4.3
Thickness (cm)	0.044	0.043	0.044	0.044	0.045
I.E.C. (meq/dgr)					
Total	3.84	3.85	3.69	3.62	4.30
Strong	1.92	1.88	1.78	1.75	2.15
Weak	1.92	1.97	1.91	1.87	2.15

*Mole % of DMAEMA replaced by (Ethyl) DEAEMA.

TABLE 4.3-II

IRON FOULING AND PERMEABILITY DATA*

Evaluation of Diethylaminoethylmethacrylate

Composition	Ethyl 25%	Ethyl 50%	Ethyl 75%	Ethyl 100%	CD1L
NP	0.25	0.25	0.25	0.25	0.25
Water Content	34.7%	35.8%	35.9%	36.8%	35.2%
Resistance (Ω-cm^2) Initial-In 0.1NHCl	5.7	4.9	5.2	4.9	4.3
In 2MFeCl with 2NHCl					
96 hrs.	17.9	24.2	36.2	60.7	15.8
192 hrs.	22.1	40.6	47.5	87.3	19.1
360 hrs.	30.7	40.6	61.5	184	18.5
Permeability* μgm Fe/hr/cm^2	14	16	12	8	14

*Data supplied by NASA-Lewis Redox Project.

4.4 Membrane Systems from Blends of CD1L with CP4L

The backup candidate resin system selected for the NASA-Redox cells has been CP4L. Membranes based on this system have withstood concentrated electrolyte solutions at temperatures up to 80°C. While the initial electrical resistance of this compound is only slightly higher than that of the CD1L, the electrical resistivity of the CP4L shows a tendency to climb in a fairly rapid manner to excessively high values.

In an attempt to combine the superior chemical inertness of the CP4L types with the greater electrical resistance stability of the CD1L types, an investigation was started on blends of the two compounds. These blends were named according to the percentage of the CP4L present. Their composition was 75% CP4L, 50% CP4L and 25% CP4L. An additional 25% blend was made which also contained some extra VBC.

These membranes were processed in the usual CD1L manner. The edge resin in the 75% and 50% CP4L blends did not exotherm markedly. The 25% variation with the extra VBC had a large exotherm. All members had a slight green cast.

These membranes were characterized for ion exchange capacity (strong and weak), water content and resistance. The results of these tests are listed in Table 4.4-I.

Membranes from each of the four sets (75%, 50%, 25% and 25% + extra VBC) were sent to NASA-Lewis for evaluation in their cells.

NASA-Lewis selected the 50% CP4L - 50% CD1L blend for their preliminary evaluation. The results of the resistance measurements in their rather extensive resistivity flow tests indicated these combination membranes would increase in resistance rapidly and extensively. Iron permeability tests run at NASA-Lewis that the 50/50 blend membrane was slightly less permeable than the CD1L membrane.

TABLE 4.4-I

MEMBRANE CHARACTERIZATION DATA

CP4L/CD1L Blends

CP4L Percent	75%	50%	25%*	25%	Typical CD1L
NP	0.25	0.25	0.25	0.25	0.25
Water Content	29.0%	32.2%	33.8%	36.5%	35.8%
Resistance 0.1NHCl (Ω-cm^2)	4.4	5.3	5.2	4.1	4.2
Thickness (cm)	0.040	0.037	0.040	0.039	----
I.E.C. (meq/dgr)					
Total	4.97	4.91	4.42	4.86	4.33
Strong	2.44	2.35	2.61	2.38	2.11
Weak	2.53	2.56	1.81	2.48	2.22

*Plus Extra VBC

4.5 Catalyst Concentration Studies

It was decided to explore the effects of catalyst concentration on the CD1L performance. Larger reduction in catalyst concentration were tried because the degree of polymerization varies as the square root of the concentration.

Preliminary 5" x 5" membranes made with reduced catalyst appeared to process in an acceptable manner and had no obvious deficiencies, therefore a full scale study was made with 10" x 11" membranes.

The range selected covered from 1% catalyst, which is twice the normal concentration down to 0.0% concentration. The five values chosen for evaluation were 0.0%, 0.0625%, 0.25%, 0.5% and 1.0%. Sets of 10" x 11" membranes were made up in the usual manner and all except the zero concentration gave relatively good leak free membranes.

The membranes produced with 0.0% catalyst were rubbery, soft and rough due to a very low degree of polymerization. Because this set was so poor only their water content was measured. The water content was about twice as high as usual. The rest of the series was characterized for water content, resistivity and ion exchange capacity measurements.

The results of this characterization are listed in Table 4.5-I. All, except the 0.0% catalyst appear to produce membranes with normal properties.

Samples from all of these runs, except the zero concentration, were checked for iron fouling in 2M $FeCl_3$ and 2NHCl. The lower concentration samples appeared somewhat less prone to fouling. Although their intial electrical resistance was not substantially different, it increased more slowly and finished appreciably lower in resistance than the members of the series with higher catalyst concentrations. The results of these tests can be found in Table 4.5-II. This table also includes some permeability data supplied by the NASA-Lewis Redox Project Group.

In addition to the catalyst studies run at 0.25 NP several sets of membranes were fabricated at 0.275 NP. The results of tests with these two NP variations were close together and both performed relatively well. On the basis of performance in actual cell stacks NASA-Lewis has now selected the 0.275 NP with 0.0625% catalyst as the prime candidate membrane system.

The use of these lower catalyst concentration, (0.0625%) should also yield membranes with:

a. less thermal stress,
b. less waste of reactants per batch,
c. membranes of superior physical properties,
d. lower catalyst cost.

TABLE 4.5-I

MEMBRANE CHARACTERIZATION

CATALYST CONCENTRATION STUDY

Catalyst Concentration	0.0%	0.0625%	0.25%	0.50%	1.0%
NP	0.25	0.25	0.25	0.25	0.25
Water Content	65-75%	36.2%	36.4%	35.8%	35.7%
Electrical Resistance 0.1NHCl (Ω-cm^2)	-	4.3	4.5	4.6	4.6
Thickness (cm)	-	0.043	0.043	0.044	0.044
I.E.C. (meq/dgr)					
Total	Under-cured Rubbery and Flexible	4.25	4.26	4.33	3.94
Strong		2.00	2.09	2.11	1.94
Weak		2.25	2.17	2.22	2.00

TABLE 4.5-II

IRON FOULING AND PERMEABILITY* DATA

CATALYST CONCENTRATION STUDY

Catalyst Concentration	0.0625%	0.25%	0.5%	1.0%
NP	0.25	0.25	0.25	0.25
Water Content	36.2%	36.4%	35.8%	35.7%
Electrical Resistance Initial In 0.1NHCl	4.3	4.5	4.6	4.6
In $2MFeCl_3$ with 2NHCl				
96 hrs.	10.5	13.5	15.7	15.5
192 hrs.	12.3	15.4	19.1	19.6
360 hrs.	12.9	14.8	18.5	19.0
Permeability* μgm Fe/hr/cm^2	20	15	14	13

*The permeability test data was supplied by the NASA-Lewis Redox Project.

4.6 Variations in Non-Polymer Content (NP)

Throughout our studies of membranes suitable for the Redox cell the importance of the NP has been highlighted. Both the quantity and the type have been shown to be important. Earlier in the program large variations in NP content were explored. These studies narrowed the range from 0.20 - 0.50 NP to 0.25 - 0.275 NP for current evaluation with the CD1L formulation, the prime candidate. Only in this range were both the resistance stability and the Fe permeability of the membranes judged satisfactory. The character of the NP has also shown itself to be important. Membranes with the most desirable properties recently have been produced only when isobutanol was used as the NP.

To check the effects of various NP's further using our most recent processing techniques, trials were made with diethylbenzene and several alcohol or alcohol blends.

DEB was selected for trial as NP as it has shown itself to be a good NP solvent in a variety of cases. For this test the 0.275 NP variation of the CD1L with the standard catalyst concentration was employed.

Despite the use of our new processing techniques for membrane fabrication the resultant monomer mix became turbid and then moderately opaque. Some separation of comonomer and adducts from NP apparently occurred during the cure and the finished membranes tended to stick to the separators. All were opaque and white at the end of the cure cycle, a certain sign of poor resin-solvent compatibility during and after polymerization, and many leaked badly when dye tested.

Because of these poor results no further work is planned using DEB as an NP for the CD1L type membranes.

Continuing the effort to reduce the resistance and/or fouling of the CD1L membrane a limited exploration of some minor variations in the NP were tried. Only alcohols were explored in this series. The alcohols chosen were all water soluble to permit rapid and inexpensive removal of the NP with water at the end of the curing sequence.

The first set of membranes (W213-80T) used tertiary butyl alcohol as the NP. Water washes rather than methanol were used to remove the NP. This was appropriate because water and tertiary butanol are completely miscible.

The second set of membranes (W213-80E) made in this study used anhydrous ethanol as the NP. Again water was used as the wash solvent. The set handled normally, but about 50% of the calendered membranes had minor leaks.

A third set of membranes (W213-80EI) fabricated for this study used a fifty-fifty blend of ethanol and isobutanol as its NP. These membranes appeared to process normally and 80% of the membranes were leak-free.

All three sets were characterized and the results along with a typical run having the standard formulation are tabulated in Table 4.6-I. The results to date do not indicate any dramatic change in properties. The only noticeably negative property observed was the high percentage of membranes with leaks when the NP was shifted to ethanol. It seems possible that, if performance in NASA-Lewis test cells so indicated, any of these membranes could be produced with acceptable yields.

Samples of these membranes were sent to NASA-Lewis to be evaluated for iron fouling and permeability. Preliminary results indicated that when t-butyl alcohol and mixed alcohol was used as NP the iron selectivity was poor. With ethanol alone as the NP the selectivity was good, however, the electrical resistance stability was below average.

Some minor variations in quantity of NP were re-evaluated. On the basis of this review the NP for the prime membrane system was adjusted to 0.275. This value was judged to give the best balance between resistance stability and permeability in cell performance tests at NASA-Lewis.

TABLE 4.6-I

CD1L-AA5 TYPE
PERMEABILITY AND
MEMBRANE CHARACTERIZATION STUDY
SOLVENT (NP) STUDY

W213-	-80T	-80E	-80ET	Typical AA5
NP	t-butyl alcohol	ethanol	ethanol/ isobutanol (50/50)	Isobutanol
NP Content	0.275	0.275	0.275	0.275
Water Content	39.6%	35.3%	37.4%	36.2%
Electrical Resistance 0.1NHCl (Ω-cm^2)	4.1	4.6	4.8	4.3
Thickness (cm)	0.035	0.035	0.039	0.040
I.E.C.				
Total	4.82	4.82	4.67	4.33
Strong	2.18	2.28	2.28	2.31
Weak	2.64	2.54	2.39	2.02
Permeability* μg Fe/hr/cm^2	38	12	25	17

*Data supplied by NASA-Lewis Redox Project.

4.7 Fabric Variations

The use of modacrylic based fabrics has become the standard for the redox cell. Membranes made with these fabrics have withstood the severe acid environments very well. Not only have they withstood the corrosive effects well but they have remained substantially unaffected at temperatures up to 80°C.

A number of other fabrics evaluated in the past have proven unsatisfactory from the cost standpoint (teflon) or chemical resistance (glass) or a variety of factors (low melting, poor adhesion, etc.). One of the more promising fabric types, however, has been polypropylene. A number of these fabrics, have been screened in the past and during the current reporting period several more were considered.

The two fabrics which received most consideration were a woven polypropylene fabric and a very light non-woven fabric treated to improve its adhesion to polar materials.

The non-woven fabric produced membranes of less than half the normal thickness. The fabric consisted of a mat of melt-blown polypropylene fibers which has been treated to make them "water-wettable". The adhesion of the polymer to the fibers appeared to be very good, however, a number of leaks occurred in these fabrics at the junction of occasional coarse fibers. Apparently these membranes cracked at these points.

The best woven polypropylene fabric was found to be excessively thick. This resulted in a rather high initial resistivity. Subsequently a calendered version of this fabric was made into membranes. While these membranes were still somewhat thicker than the calendered modacrylic they were screened and several sent to NASA-Lewis for their examination.

The results of the characterization and static permeability test are listed in Table 4.7-I.

TABLE 4.7-I

FABRIC VARIATIONS

CHARACTERIZATION AND PERMEABILITY

CD1L-AA5

W233-12

Fabric Composition	Modacrylic	Polypropylene
NP	0.275	0.275
Water Content (%)	36.2%	35.7%
Electrical Resistance 0.1N HCL (Ω-cm^2)	4.3	5.3
Thickness (cm)	0.036	0.051
I.E.C. (meq/dgr)		
Total	4.72	4.49
Strong	2.06	2.22
Weak	2.66	2.27
Permeability µg Fe/hr/cm^2 0.5N HCl/1 M $FeCl_3$	17.3	16.7

4.8 Cross-Link Study

In our work to reduce the initial and the in-service resistance of the redox membranes a study of the effects of a variety of cross-linking monomers, capable of copolymerizing with the DMAEMA, was undertaken. Most of these monomers were acrylates having functionalities of from two to four. While many of the polymers made did not contain any VBC several formulations maintained substantial percentages of VBC.

The first series was composed of blends of VBC and a long difunctional acrylate (1,6 hexanedioldimethacrylate). The results of the characterization and evaluation tests on these membranes can be found in Table 4.8-I. The results of NASA's tests did not show any improvement either in resistance stability or permeability. It had been thought that decreases in the VBC contents of the system might reduce the rise in resistance that occurs as the membranes stand in contact with $FeCl_3$/HCl solutions.

The whole study maintained DMAEMA as the amine containing comonomer (as does the CD1L). The series depicted in Table 4.8-I maintained a 2 mole to 1 mole ratio of DMAEMA to cross-linker. Both the long difunctional compound and the trifunctional compound in this series gave results not greatly different than the CD1L. One point worthy of note was that the elimination of the aromatic VBC for aliphatic long difunctional cross-linkers did not reduce the build up of fouling resistance in NASA's test over the members of the series with 25 or 50% VBC.

A second part of the cross-linking study maintained a constant amount of DMAEMA, a constant NP but maintained only a constant volume of cross-linker. The cross-linkers were difunctional, trifunctional and tetrafunctional acrylates and methacrylates. The polymers formed were evaluated by the NASA-Lewis Redox Unit for permeability and resistivity flow. The results of the characterization tests and NASA's tests are shown in Table 4.8-II.

The tests indicate that lower cross-link density systems yield polymers with better resistance stability but much poorer selectivity (higher iron permeability). The relatively low molecular weight of VBC gives it a distinct advantage in these compositions by allowing more moles of ionic functionality per unit volume.

The polymers in both phases as shown in Tables 4.8-I and 4.8-II, gave membranes that appeared to behave and process in a normal manner.

The membrane formulations in Table 4.8-II which maintain a constant volume of DMAEMA were also examined as a function of available cross-linking sites. As in the case of Table 4.8-I, Table 4.8-II is on a basis of 2 moles of DMAEMA per mole of cross-linking. All of the cross-linking in Table 4.8-II is thru vinyl group while some of the cross-linking in Table 4.8-I is ionic (VBC) and some thru vinyl groups.

Generally, the results indicate that a ratio of two moles of DMAEMA to about 1 mole of XL is a desirable one. On the basis of permeability, difunctional molecules generally appear to react more fully than the tri and tetrafunctional ones. Also it appears that the permeability increases rapidly at the low cross-link densities. From the data developed one could not conclude that there was any dramatic difference in the effect of ionic cross-links as compared with the vinyl cross-links.

Theoretical unit weight per cross-link was calculated for several of the compounds. They are listed below:

	DMAEMA MOLES	MOLES XL	CALCULATED MOL WT PER/XL
VBC	2	1	466 g (CD1L Prime Candidate)
1,6 Hexanedioldi-methacrylate	2	1	568 g (Long Di Funct. 4.8-I)
1,6 Hexanedioldi-methacrylate	2	0.55	825 g (Long Di Funct. 4.8-II)
Pentaerithatol-tetraacrylate	2	1.42	399 g (Tetra Funct. 4.8-II)

While generally it can be said that the lower the molecular weight per cross-link the lower the permeability, a number of other factors (steric hinderance, NP types and amount, etc.) have a significant effect on the actual parameters of permeability and fouling resistance.

TABLE 4.8-I

CROSS-LINKING STUDY

EVALUATION DATA*

(2 Moles Amine - 1 Mole Cross Linker)

Composition XL	100% Long Difunctional	50% Long Di 50% VBC	25% Long Di 75% VBC	Trifunctional 100%
NP (IBUOH)	0.275	0.275	0.275	0.25
Water Content	32.0%	35.4%	36.9%	34.4%
*Resistance (Ω-cm^2)	27	22	23	17
R in 0.1N HCl (Ω-cm^2)	4.2	4.2	4.4	9.8
I.E.C. Content (meq/dgr) Total	3.82	4.35	4.42	3.44
*Permeability Test µg Fe/Hr/cm^2	30	27	25	17

*Test values for resistance and permeability were supplied by NASA-Lewis Redox Project.

Note: Di= Difunctional

TABLE 4.8-II

CROSS-LINKING STUDY

EVALUATION DATA*

DMAEMA Constant By Volume
XL Constant By Volume

Composition XL	Long Di	Tri-Funct.	Short Di	Tetra Funct.	50% Tetra 50% Di	Tetra Blend	Medium Di
NP	0.275	0.275	0.275	0.275	0.275	0.275	0.275
DEB						(IBUOH)	(IBUOH)
Water Content	29.8%	32.3%	34.1%	37.9%	36.4%	30.5%	28.4%
Resistance Test*	4.3	4.9	4.9	8.1	7.0	14	-
R in 0.1N HCl (Ω-cm^2)	3.2	4.1	4.0	4.0	3.2	3.8	3.0
I.E.C. Content (meq/dgr) Total	4.92	4.75	4.85	4.80	4.65	4.45	4.54
Permeability* Test	179	81	75	66	81	37	-
XL Mole Sites/ 2 Moles DMAEMA	0.55	0.877	0.745	1.42	1.08	0.934	-

*Test values for resistance and permeability were supplied by NASA-Lewis Redox Project.

Note: Di= Difunctional.

5.0 Static Permeability Tests

The permeability of the anion membranes to the Fe ions is an important characteristic of membrane performance. Their ability to keep the iron solution and the chromium solution from mixing materially affects the life of the battery. Because of this, measurements of Fe ion permeability have become one of the primary criteria for selection of anion membranes for use in the redox cell.

In the past Ionics has utilized a permeability test cell wherein a Faraday of electricity was applied at a certain current density and the amount of iron passing thru the membrane measured by u.v. absorbtion. During this reporting period in response to NASA's suggestion another test setup was made in which a static diffusion cell was employed. This cell, which does not use electric current as a driving force for the ions, has been developed and utilized by NASA as a screening test.

This static diffusion test is faster and simpler to run and has been shown by NASA to have good correlation with performance in the small Fe/Cr electrical cell.

It was decided Ionics would use these static diffusion cells for screening to permit more time to be spent in the preparation of membranes. Accordingly several cells of this type substantially identical to those used at NASA-Lewis were made up and put into service in the latter part of the contract period. One of these cells was made from "Lucite" and the other four from "Lexan".

The results of a limited number of tests made with these cells gave results generally consistent with those of NASA-Lewis. In addition to these room temperature tests some tests were run at 50°C.

In the few elevated temperature static diffusion tests run, the permeability values were scattered and higher. A limited investigation of the results indicated better gasketing between the face of the cell and the membrane would be essential to higher accuracy and reliability.

GLOSSARY

IBUOH - Isobutylalcohol

VBC - Vinylbenzylchloride

DEB - Diethylbenzene

DMAEMA - Dimethylaminoethylmethacrylate

DEAEMA - Diethylaminoethylmethacrylate

4-VP - 4-Vinylpyridine

TMP - Trimethylolpropanetrimethacrylate

NP - Non-Polymer Content

CD1L - #1 Candidate Membrane System - Copolymer of VBC and DMAEMA

CP4L - Candidate Membrane System - Copolymer of 4-VP and DVB

IEC - Ion exchange capacity (meq/dry gram resin)

Permeability - measured in 1.5M $FeCl_3$ with 0.5N HCl - μg of $Fe/hr/cm^2$

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16. Abstract

The efforts on the synthesis of polymer anion redox membranes for the period covered in the report, were mainly concentrated in two areas, membrane development and membrane fabrication. The first of these areas, membrane development, covered the preparation and evaluation of experimental membranes systems with improved resistance stability and/or lower permeability.

The experimental membranes prepared and evaluated in the first area fell into several general groups or series. One such series was a number of variations made in the formulation and preparation of the prime candidate CDIL system.

These variations encompassed changes in NP quantity and type and changes in the ratio of the monomers used to make the membrane polymer. Similarly cure and catalyst studies along with the use of various new fabrics were explored - as well as blending various percentages of the number one and number two candidate polymer systems.

Another facet of the exploratory program produced membranes using other cross-linking agents and blends of cross-linking agents.

The second area of activity, membrane fabrication, covered the laboratory scale production of prime candidate membranes in quantities of up to two hundred and sizes up to 18 inches x 18 inches (46 cm x 46 cm). These small (10" x 11") and medium sized membranes were mainly for assembly into multicell units. Improvements in processing procedures and techniques for preparing such membrane sets have lifted yields to over 90%.

The formulations chosen for application in this phase of the program, were of the CDIL type. The scaled up candidates were in the 0.25 to 0.0275 NP range. The latest prime candidate membrane system has an NP of .275 and is made with a greatly reduced catalyst level. Preliminary results indicate such membranes give substantially improved performance in multicell stacks. Such membranes have been used by NASA-Lewis to make four 40 cell pair stacks which have a one to three kilowatt capacity.

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