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ANION PERMSELECTIVE MEMBRANE

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To: NASA-Lewis Research Center

Cleveland, Ohio 44135

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A Summary Report
Anion Permselective Membrane
DEN 3-1

Submitted by: Research Division

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FORWARD

This document constitutes the final report for the work accomplished

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ION SELECTIVE SEMIPERMEABLE ANION EXCHANGE MEMBRANES.

Dr. Russell B. Hodgdon provided overall program management. The principal

investigators were Samuel S. Alexander and Warren A. Waite with major contribu-

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ABSTRACT

Experimental composite membranes were synthesized on a lab scale consisting of a thin layer of anion permselective resin supported by and bonded to a porous physically strong and conductive substrate film. These showed good selectivity and also substantially lower electrical resistivities than the homogenous candidate membranes optimized in the previous contract.

A wide range of resin porosities were examined for three candidate membrane systems, CD1L, CP4L, and A3L to identify the formulation giving the best overall redox cell performance. The objective was to obtain the optimum membrane porosity giving an acceptable selectivity and long range resistance stability in redox cell operation.

Candidate anion membranes showed large increases in resistivity after a short time of immersion in conconcentrated $FeCl_3$/HCl solution. The resistance rise was attributed to exchange site fouling by the complex ions $FeCl_4^{-1}$ and $FeCl_6^{-3}$ and was found to be reversible by HCl washing.

Limited quantities of two candidate membranes CD1L and CP4L (in the 10" x 10" size) were made up using several fabrics and various N.P. contents from 25 to 33%. Largely on the basis of resistance stability the CD1L formulation was selected as prime candidate and about thirty-five membranes (one foot square) were produced for experimental static and dynamic evaluation.

A better appreciation of the significance of the various processing parameters was gained during this study. This improved understanding permitted us to increase the batch size and therefore the number of membranes per batch, while making substantial improvements in both uniformity and reliability.

1.0 INTRODUCTION & SUMMARY

Contract DEN3-1, <u>The Development of Improved Ion Selective Membranes</u> represents a continuation of the work begun under NAS 3-18897 and NAS 3-20108 to synthesize and evaluate experimental anion permselective membranes useful as cell separators in a redox power storage system being developed at the NASA Lewis Research Center. In the earlier effort many candidate and alternative membrane systems were investigated from which at least five showed good to excellent physical and electrochemical properties essential for viable redox cell operation. These were:

High selectivity-minimum transfer in the range of $1-8x10^{-3}$ mg Fe/mF

Low electrical resistivities 2-6 Ω-cm^2 in 1N HCl

Good 1000 hr durability in the redox environment at 80°C

Capability for manufacture scale up to 1.8 ft^2

Potential for further significant improvement remained primarily in the area of membrane resistivity and its long term resistance stability during cell operation.

Membrane electrical resistance is a direct function of the membrane fabric thickness. By reducing membrane gauge through the use of lightweight thin fabric support, substantial reduction in resistance was demonstrated for the various candidate systems. However, the membrane gauge was limited to films greater than 0.10mm due to the inherent fragility of the homogeneous polymer and variable fabric/polymer compatibility.

Under DEN 3-1 further substantial decrease in membrane resistance was achieved by the synthesis of composite "skin" membranes, a novel type of membrane consisting of a thin polymeric film of anion exchange resin supported on and bonded to a porous substrate material. Composite membranes were made showing good selectivity and electrical resistances

1/5 to 1/2 of that of the optimized candidate membranes prepared in the previous contract period. The film forming or coating solutions were composed of monomers and polymers of vinylbenzyl chloride (VBC), 4 vinyl-pyridine (4 VP) dimethylaminoethyl methacrylate (DMAEMA) and tetraethylene pentamine (TEPA). These were applied singly or in combination by spraying or dipping to a variety of substrates. The overlay functional films were in most cases similar in composition to the candidate membrane systems CD1L and CP4L. The substrates tried were aminated polyvinyl chloride film, macroreticular anion membranes, and microporous polyvinylchloride. The most successful and reproducible composite membranes were prepared on 2 mil aminated PVC substrate.

The current program also investigated a wide spectrum of resin porosities for 3 preferred candidate membrane systems: A3L, CD1L, and CP4L. Different porosities were obtained by varying the non-polymer solvent content (N.P.) of the polymerizate over the range of 25 to 50%. The objective of the study was to identify the optimum formulation for improved redox cell performance with respect to long term cell and resistance stability and cell capacity. A major problem in redox cell operation has been the steady and large increase with time of the cell resistance. This has been related to fouling of the membrane's ion-exchange groups by the complex anions $FeCl_4^-$ and $FeCl_6^=$. The membranes optimizied for selectivity and possessing the lowest porosities have shown the greatest susceptibility to resistance increases with time of cell operation. Conversely, porous membranes with poor selectivity have shown long term resistance stability but at the cost of high cross mixing of the reactive cations. Selectivity and resistance data indicate that the optimum membrane in any candidate system will require a compromise between an acceptable cell stability in terms of iron/chromium mixing and a reasonable long term stability for the cell resistance.

As the selection of CD1L or CP4L for scale up became more certain it became necessary to concentrate on the processing details of these distinctive resin blends. During mixing of these monomers substantial viscosity increases occur due to the formation of charged quarternary ammonium adducts. The impregnation of the fabrics with these adducts poses an essentially new processing problem as they are constantly changing in viscosity and to some degree in wetting characteristics. This viscosity increase is caused by fixed ion repulsion along polymer backbones.

1.1 SUMMARY OF RESULTS

1. The CD1L membranes have been found to possess

   (i)   relatively low initial resistance

   (ii)   good resistance stability

   (iii)   good selectivity

   (iv)   relatively good life in the redox environment

The CD1L-A5 formulation at a non-polymer solvent content (f_{NP}) of 0.25 appears

to have optimum balance between conductivity and low iron permeability.

2. The preparation of ionically crosslinked membranes having high conductivity,

high selectivity and relatively high resistance stability can now be done with

yields of 60% to 80% by adjusting reaction conditions so as to slow down

the formation of high viscosity monomer adducts during the tray laying process.

3. The problem of the steady and large increase of a redox cell's resistance

with time appears to be related to fouling. A major source of fouling is the

membranes absorption of the complex $FeCl_4^-$ and $FeCl_6^=$ anions. Membranes

with low permeability tend to foul more rapidly than those with high

permeability.

4. At this time a variety of membranes have been tested in the redox solutions

at temperatures up to $80^{\circ}C$. Among those types tested were:

A3L-B7

CD1L-A5N

103QZL-5

CP2L

CP4L

The CP4L had very good chemical stability in both Fe^{+3} and Cr^{+3} at $80^{o}C$. Its electrical resistance stability however was marginal.

The CD1L had good chemical stability in Fe^{+3} at $80^{o}C$ but poor chemical stability in Cr^{+3} at $80^{o}C$. Its electrical resistance stability however was markedly superior to the CP4L.

5. A variety of composite membranes were fabricated by applying coatings to porous substrates. The most successful coatings were CD1L and CP4L types applied to an aminated polyvinylchloride film and a macroreticular anion membrane. Membranes of this type can have resistances of less than one ohm-cm^2 and still exhibit very low permeability. The best on the macroreticular base was difficult to reproduce. These systems however are intriguing because of their ability to produce coatings of generally acceptable selectivity at minimum resistance.

2.0 COMPOSITE MEMBRANES

The composite "skin" membrane is a two component structure; a thin film or coating of ion selective polymer chemically bonded to a physically strong conductive porous substrate. The thin polymeric film of dense anion exchange resin functions as the perm-selective component which minimizes the transfer and mixing of the reactive cations while the porous substrate component imparts the necessary physical strength but offers little or no resistance to the passage of ions.

The composite membrane conductivity depends primarily on the film gauge and concentration of ionizable groups in the functional anion overlay film. The composite membrane system, because of the high film strength of the porous substrate, has the advantage of allowing the formulation of a viable thinner anion selective film than would be physically possible for the homogenous fabric backed membranes.

2.1 COMPOSITE MEMBRANE SYSTEM CM-VC

The composite membrane system CM-VC consists of a polymeric anion selective coating bonded to polyvinyl chloride (PVC) film which was pre-aminated to create a porous conductive substrate. The polymeric coatings were composed of various combinations of monomers and polymers used in the manufacture of the candidate membrane systems CD1L and CP4L. These were the monomers vinylbenzylchloride (VBC), 4-vinylpyridine (4 VP) and dimethyl amino-ethyl methacrylate (DMAEMA) and their respective linear polymers.

The substrate was prepared by aminating 2 mil commercial PVC film with tetraethylene pentamine (TEPA) at elevated temperatures yielding a porous but physically strong amber-colored film containing primary and secondary amino and unreacted chloro groups. The substrate film properties were:

weak base IEC	3.5 - 4.5 meq/dgr
water content	35 - 45%
Fe^{+3} transfer, P_{Fe}^+	2 - 10 mg Fe/mF
Electrical resistivity R_P^J (in 1N HCl)	.010 - .020 $\Omega\text{-cm}^2$

Before application of the polymer coating the substrate films were pretreated in either of two different ways: (i.) Saturated in propylene-glycol. (ii.) Hardened and preshrunk in hot $FeCl_3$. These pretreatments served to prevent excessive drying and shrinking of the film during the heat cure cycle and also tended to inhibit diffusion of the monomers and polymers into the body of the film.

In most cases the "skin" of the composite membrane was applied to the substrate film by standard spraying techniques. The film forming solutions used were in the range of 1.5 to 5.5% in total solids. Brief exposure of the solvent coated film to air at room temperature allowed the volatile solvent to flash off leaving a thin film of reactive monomer/polymer on the substrate surface.

Polymerization reactions should occur on the substrate surfaces as the solvent evaporates, with the reactive coating monomers reacting with each other and also with the chloro and amino groups present in the substrate to form a continuous surface polymer "skin" bonded to the substrate base.

Following air drying of the applied skin, the coated areas were heat cured with short exposure to a lamp which served to complete the polymerization of the unreacted vinyl, amino and chloro groups.

In general, two to three consecutive coating applications and heat cures were found effective in this system (Table I).

The polymer/monomer combinations which produced composite membranes with good selectivity and electrical resistivities below 4.0 $\Omega\text{-cm}^2$ were the following (Table I).

i.   Poly VBC, DMAEMA monomer

ii.   Poly VBC, 4VP monomer

iii.   DMAEMA, VBC monomers

iv.   4VP, VBC monomers

Five other unsuccessful combinations are included in the summary shown in Table II.

The composite membranes represented by (iii.) Table I, were prepared by dip coating one surface of the substrate film in an aqueous solution of VBC-DMAEMA dimer and DMAEMA monomer. High viscosity coating solution, 300 cps (which resulted from partial polymerization of the monomers), required only one application to achieve good selectivity. In the same system, four applications of a low viscosity coating solution (6 cps) were needed to obtain a comparable low transfer of Fe^{+3}.

Most of the composite membranes synthesized in the CM-VC system showed reasonably constant values for Fe^{+3} transfer after repeated cycling in acid

TABLE I

COMPOSITE MEMBRANE SYSTEM CM-VC

Effective Coating Compositions

Substrate – 2 mil PVC Film Aminated with TEPA

Coating Composition	Substrate Pretreatment	Application	Composite Properties		Comment
			Fe^{+3} Transfer P^+_{Fe} (mg Fe/mF)	Resistivity R^J_e ($\Omega\text{-cm}^2$)	
None	Substrate Only	None	2.0 – 10.0	0.10–0.20	Porous film – High Fe^{+3} transfer, low resistivity.
i Poly-VBC, DMAEMA	Saturated in Propylene Glycol	Spray with low solids solution IR Lamp cure	0.04 – 0.05	0.38–0.45	Good reproducibility – scaled up to 100 cm^2 area.
ii Poly-VBC, 4VP	Saturated in Propylene Glycol	Spray with low solids solution, IR lamp cure	0.017– 0.078	0.59–0.97	Fair Reproducibility – Scaled up to 100 cm^2 area.
iii DMAEMA, VBC	Hardened in Hot $FeCl_3$	Dip coating in high solids solution, oven cure	0.025– 0.067	0.85–0.98	Low to high viscosity solutions effective, CD1L-A5 formulation.
iv 4VP, VBC	Saturated in Propylene Glycol	Spray coating with low solids solution, IR lamp cure	0.054	0.46	Promising composite, CP4L-A2 formulation.

*See Table III

T A B L E   I I

SUMMARY - VIABLE COMPOSITE MEMBRANES

AS A

FUNCTION OF COATING SYSTEMS AND SUBSTRATES

Coating Systems Polymer/Monomer Components	Substrates		
	PVC Film	Macroreticular Anion Membrane	Microporous PVC Sheet
a) Poly VBC	NE	B	B
b) Poly VBC, DMAEMA	A	NE	-
c) Poly VBC, VBC, DMAEMA	-	NE	-
d) Poly VBC, VBC, 4VP	-	NE	-
e) Poly VBC, Poly DMAEMA	NE	B	NE
f) Poly VBC, 4VP	A	B	B
g) Poly VBC, Poly 4VP	NE	NE	NE
h) Poly DMAEMA	-	NE	NE
i) Poly DMAEMA, VBC	-	NE	NE
j) Poly 4VP	NE	NE	NE
k) Poly 4 VP VBC	NE	NE	NE
l) DMAEMA, VBC	A	B	-
m) 4VP, VBC	A	-	-

Key:
     A = Good Properties, Reproducible
     B = Shows Promise, Fair Reproducibility
    NE = Not Effective

and concentrated $FeCl_3$ solution. This indicated the applied "skin" coatings were firmly and durably bonded to their respective substrate base.

The largest composite membrane prepared was approximately 100 cm^2 in area (10 x 10 cm). The composite membrane CM-VC showed good potential for scale-up and manufacture.

2.2 COMPOSITE MEMBRANE SYSTEM CM-MR

The composite membrane system CM-MR consists of an anion selective polymer coating bonded to an anion macroreticular membrane as the substrate film. Macroreticular resin is a highly porous crosslinked resin network, prepared   by polymerizing monomers in the presence of a solvent having low solubility for the forming polymer. The phase separation of polymer and solvent during polymerization produces large islands or spaces in the resin matrix, having $500\overset{\circ}{A}$ to $1000\overset{\circ}{A}$ pore diameters.

Only one coating composition method was found effective in creating a composite with acceptably low Fe^{+3} transfer (Table III). This was a spray coating using a dilute solution of poly VBC and 4VP monomer to yield a composite membrane with Fe^{+3} transfer rate P_{Fe}^{+}, of 0.020 to 0.028   mg Fe/mF and resistivity R_{ρ}^{J} of 0.77 Ω-cm^2.

Two other coating formulations showed some promise. These were:

(i.) Dip coating of dilute solution poly VBC
followed by soaking of the composite
in TEPA to increase the amine content of the
skin component.

(ii.) Spray coating of DMAEMA and VBC monomers.

Thus far a major drawback of this system has been the lack of reproducibility of functional properties of the composite.

COMPOSITE MEMBRANE SYSTEM CM-MR

Effective Coating Compositions

Substrate - Macroreticular Anion Membrane, reacted with TEPA,
Coating applied to dry substrate, oven cured at 80°C

Coating Composition	Application	Post-Treatment of Composite	Composite Properties		Comment
			Fe^{+3} Transfer P_{Fe}^+ (mg Fe/mF)	Resistivity R_ℓ^J ($\Omega-cm^2$)	
None	None	Substrate Only	2.0	0.97	High Porosity Resin
Poly-VBC	Dip coating with dilute solution	Soaked in TEPA	0.25 – 0.48	0.78 – 0.81	Reproducibility fair – selectivity improvement by additional coating
	Spray coating with dilute solution	None	0.33	0.83	Same as above
Poly-VBC, 4VP	Spray coating with dilute solution	None	0.020 – 0.028	0.77	Good selectivity, poor reproducibility
DMAEMA, VBC	Spray coating with dilute solution	None	0.55 – 0.59	0.71 – 0.73	Promising, improvement in selectivity by additional coatings

Other anion macroreticular membranes were evaluated on standard and thin fabrics (modacrylic) for use as the substrate film. In one study the macroreticular boards with pendant $-CH_2Cl$ groups were reacted with a series of amines to observe the effects of the various amines on the total system. The amines used were tetraethylenepentamine, diethylenetri-amine, and trimethylamine.

Composite specimens were prepared (Table IV) by coating this DETA MR membrane with CD1L-A5 mix. These CD1L-A5 coatings produced no significant improvement in performance.

Another set of membranes was made by coating the unreacted macro-reticular boards, each having pendant $-CH_2Cl$ groups, with the CD1L A5 (VBC-DMAEMA) adduct solution. This five day old solution was about 100 cps in viscosity at the time of application to the board. Unfortunately, after curing and treatment with 1N HCl, tests on the resultant membrane showed that meaningful reductions in permeability were accompanied by significant increases in resistance.

CD1L-A5 Topcoat Macroreticular Base	1N HCl Resistance	mg/mF Fe Permeability
22 mil Modacrylic	$0.85 \ \Omega\text{-cm}^2$	0.136 - 0.141
Thin Fabric	$10.1 \ \Omega\text{-cm}^2$	0.002 - 0.010

Work on the macroreticular composite membranes to date has indicated two factors may be very critical.

1.) Initially good composite membranes often lose their selectivity

T A B L E   I V

QUATERNIZATION OF DVB-VBC MACRORETICULAR BOARD

Standard Fabric

Amine Reactant	Thickness	Water Content	I.E.C. Capacity (meq/gdr)
TEPA	0.050 cm	57.2%	2.10
DETA	0.053 cm	57.2%	2.70
TMA	0.050 cm	60.0%	1.91

Thin Fabric

TEPA	0.037 cm	54.4%	1.95
DETA	0.037 cm	56.7%	2.38
TMA	0.034 cm	58.0%	1.87

because their surface film loses its adhesion to the substrate and is washed away.

    2.) Thick films apparently block the pores of the membrane and yield composites having excessive resistance.

    The production of effective, practical composite membranes will require the deposition of very thin anion films which have excellent adhesion to their substrates.

2.3 COMPOSITE MEMBRANE CM-MPV

In composite membrane system CM-MPV the substrate material was a microporous PVC filter sheet 20 mil in thickness with 0.1µm pore size. The untreated highly porous film showed an extremely high Fe^{+3} transfer rate (28 mg Fe^{+3}/mF) at a resistivity of 0.71 Ω-cm^2.

Two coating formulations showed promise by reducing the Fe^{+3} loss to the region of 1 mg Fe/mF. These were:

> (i.) A solvent cast film of poly VBC containing triethylphosphate.
>
> (ii.) Spray coating of poly VBC and 4-VP monomer.

A major drawback of this composite system was the inability to obtain sufficiently low selectivity. Reproducibility of fabrication was also a problem.

3.0 POROSITY VARIATION IN CANDIDATE MEMBRANES

A major problem in redox cell performance has been cell resistance instability. Large undesirable increases in cell resistance have been associated particularly with candidate membranes synthesized for low porosity and high selectivity. The resistance increase in these membranes is most likely caused by fouling of the resin exchange sites by attachment to them of the complex anions $FeCl_4^-$ and $FeCl_6^{-3}$. Static tests with membrane strips have demonstrated dramatic rises in membrane resistance on short contact with $FeCl_3$/HCl solutions. (Table V).

It was also observed that less selective and more porous membranes have performed with greater resistance stability. This is due to the diffusion of more electrolyte into the resin matrix, which results in a larger fraction of the electrical conductance being carried by the diffusing ions (H^+ and Cl^-) and thereby diminishing the resistive influence of the fouled ion exchange sites. In these cases the cell resistance stability is obtained at the cost of high cross-mixing of the reactive cations with resultant higher diffusion of iron and chromium in the cell.

Optimization of selectivity by itself was found to be counter productive to achieving long term resistance stability for the redox cell. Synthesizing the optimum membrane in any candidate system may require a compromise between an acceptable level of cross diffusion (cell capacity) and a reasonably stable cell resistance.

To determine the optimum membrane formulation a wide spectrum of resin porosities was synthesized by incorporating different amounts of non-polymer (NP) solvent in their manufacture. The NP solvent fraction f_{NP}, of the polymerizates was varied over the range of 0.25 to 0.50 for three of the preferred candidate membranes A3L-B7, CD1L-A5, and CP4L-A2. The membranes were prepared on 22 mil modacrylic and where possible on thinner lightweight modacrylic fabric. A

MEMBRANE RESISTIVITY IN $2MFeCl_3$ AND VARIABLE HCl CONCENTRATION

Membrane Resistivity, R_ρ^c, $(\Omega-cm^2)$

Membrane		Treatment	Normality of HCl in Test Solution						
			0.5N	1.0N	2.0N	3.0N	4.0N	5.0N	6.0N
A3L–B7 (Anion)	I	Original memb., measurement in HCl only	5.8	3.0	2.6	2.1	2.0	2.2	2.9
	II	Exposure to 2M $FeCl_3$/HCl for 24 hours	25.8	43.1	57.8	65.2	43.1	67.7	70.1
	III	Exposure to 2M $FeCl_3$/HCl for 700 hours	62.7	68.9	73.8	73.2	80.0	65.2	59.7
	IV	Regenerated in 1N HCl, measured in HCl only	8.9	7.6	4.4	3.2	2.4	3.0	3.3
CP4L–A2N (Anion)	I	Original memb., measurement in HCl only	2.9	2.5	2.1	1.4	1.3	1.6	1.7
	II	Exposure to $2MFeCl_3$/HCl for 24 hours	17.3	57.6	67.7	62.1	54.7	57.4	52.9
	III	Exposure to $2MFeCl_3$/HCl for 700 hours	43.7	66.4	73.8	83.6	59.0	27–74	26–74
	IV	Regenerated in 1N HCl, measured in HCl only	3.1	2.6	1.8	1.4	1.3	1.0	1.2
CD1L–A5N (Anion)	I	Original memb., measurement in HCl only	3.8	2.2	1.4	1.1	1.1	1.1	1.0
	II	Exposure to 2M $FeCl_3$/HCl for 300 hours	10.6	20.1	44.3	94.7	54.8	38.1	59.0
103QZL–S (Anion)	I	Original memb., measurement in HCl only	4.5	2.9	1.5	1.3	1.2	1.2	1.1
	II	Exposure to 2M $FeCl_3$/HCl for 300 hours	8.2	.7.3	.6.5	5.5	5.4	4.4	4.2
61CZL (Cation)	I	Original memb., measurement in HCl only	1.0	1.0	0.9	0.9	0.8	0.8	0.8
	II	Exposure to 2M $FeCl_3$/HCl for 24 hours	7.4	4.3	2.8	2.3	1.8	1.5	1.4
	III	Exposure to 2M $FeCl_3$/HCl for 700 hours	6.6	4.0	2.4	2.2	2.0	1.5	2.0

Resistance of membrane samples measured directly on removal from test solution by means of contact probes an A.C. resistance bridge at 1000HZ. Contact probe area = 0.123 cm^2.

MEMBRANE PROPERTIES AS A FUNCTION OF NON-POLYMER SOLVENT CONTENT

Membrane	f_{NP}	IEC (meq/dgr) Total	Strong	Weak	H_2O Content %	Film Thickness (mm) A	B	Resistivity R_l^J in 1.0N HCl (Ω-cm^2) A	B	Fe^{+3} Transfer, P_{Fe}^+ (mg Fe/mF x 10^{-3}) A	B
A3L-B7	0.25	3.40	--	3.40	32.0	0.60	--	6.45	--	1-2	--
A3L-B7N	0.35	3.45	--	3.45	39.0	0.60	--	4.16	--	40-140	--
CD1L-A5	0.25	4.15	2.18	1.97	31.0	0.60	0.12	4.19	2.50	5-8	5-8
CD1L-A5N	0.35	4.38	2.03	2.35	41.6	0.60	0.12	2.95	1.77	5-7	110
CD1L-A5P	0.40	4.52	2.05	2.45	43.9	0.60	0.12	2.62	1.10	33-38	220
CD1L-A5Q	0.50	3.94	1.88	2.07	43.3	0.60	0.12	2.37	1.21	53-61	230
CP4L-A2	0.25	5.30	2.94	2.36	31.8	--	0.25	--	2.15	--	4-8
CP4L-A2N	0.35	5.89	--	--	32.9	0.60	0.18	3.34	2.67	4	30-34
CP4L-A2P	0.40	5.69	2.78	2.91	38.6	0.60	0.18	2.66	2.04	14-18	36-57
CP4L-A2Q	0.50	5.35	2.38	2.97	47.7	0.60	--	1.58	--	250	---

Key: f_{NP} = fraction of non-polymer solvent in monomer solution.
A = 22 mil modacrylic fabric
B = Modacrylic fabric backing M100
A3L-B7 = Copolymer divinylbenzene and 2-vinylpyridine
CD1L-A5 = Copolymer vinylbenzyl chloride and dimethylaminoethyl methacrylate
CP4L-A2 = Copolymer vinylbenzyl chloride and 4-vinylpyridine

summary of the analyzed membrane properties is given in Table VI.

As anticipated, water content increased with increasing values of f_{NP} but the Fe^{+3} transfer rate, P_{Fe}^{+}, showed variable increase depending on the polymer system and fabric backing. In the CD1L-A5 system, the 22 mil modacrylic backed samples maintained good to fair selectivity over the entire f_{NP} range of the series. The modacrylic (M-100) backed membranes did not show gross leakage by dye testing but the Fe transfer was excessive and may indicate poor resin fiber bond for this fabric. However the modacrylic (M-100) fabric appears to work as well as the 22 mil modacrylic at the lowest f_{NP} level (0.25).

The CP4L-A2 membranes showed low Fe transfer at all f_{NP} values except at the extreme end ($f_{NP} = 0.50$). The A3L-B7 system ceased to give good selectivity at $f_{NP}=0.35$. The superior selectivity performance of the CD1L-A5 and CP4L-A2 at the higher porosities was due to the large ion exchange capacity (IEC) of the resins.

Samples of the above membranes which gave Fe transfer rates less than 0.100 meq Fe/mF were sent to NASA labs for testing.

On the basis of tests conducted at NASA Lewis Center, seven different batches of homogenous candidate membranes were ordered and delivered to the center. These were prepared on 22 mil and thinner woven fabric backings.

These were the:

1. CD1L-A5H
2. CD1L-A5
3. CD1L-A5P
4. CP4L-A5P
5. A31-B7
6. A4L-28A
7. 103QZL-S

The analyzed properties are summarized in Table VII.

T A B L E V I I

CANDIDATE MEMBRANES - PILOT SCALE PRODUCTION

Manufactured Membrane Area - 9" x 10"

Membrane	Number Delivered	Modacrylic Backing	Thickness (mm)	R_e^{J*} $\Omega\text{-}cm^2$	IEC (meq/dgr)	% H_2O
103QZL-S	20	Standard	0.60	4.1	2.19	37.4
CD1L-A5H10	6	Standard	0.60	---	4.00	32.6
CD1L-A5H10	3	Thin	0.30	---	4.00	32.6
A3L-B7P	6	Thin	0.30	---	3.21	29.4
CD1L-A5P	6	Standard	0.58	2.50	4.18	43.9
CD1L-A5P	6	Thin	0.32	2.16	4.18	43.9
CP4L-A2P	6	Thin	0.32	----	4.90	39.0
A4L-28A	12	Standard	0.60	2.33	4.36	46.7
CD1L-A5	5	Thin	0.30	4.06	4.35	35.9
CD1L-A5	2	M-100	0.12	1.96	4.35	35.9

*1N HCl

4.0 MEMBRANE RESISTIVITY IN FeCl$_3$ AND VARIABLE HCl CONCENTRATION

The effect of 2M FeCl$_3$ on the resistivity of anion and cation membranes was studied as a function of HCl acidity in the range of 0.5 to 6N under static non transfer conditions. Sample strips of various anion membranes and one cation membrane were immersed in 2M FeCl$_3$ solutions adjusted with HCl then measured for resistivity, $R\rho^c$, directly on removal from solution using contact probes and an AC resistance bridge. The test strips were also measured in HCl alone before FeCl$_3$ immersion and after regeneration in 1N HCl. The membranes tested were the anions A3L-B7, CD1L-A5N, 103QZL-S (standard) and the cation 61CZL. The results are summarized in Table V.

At 24 hours the resistivity of the A3L-B7 and CP4L-A2N membranes increased from 5 to 30 times higher than the original resistance in the respective HCl solution without FeCl$_3$, with the greater increases occurring above 2N HCl. At 700 hours in FeCl$_3$ the resistivities at the lower acidities tended to rise to the higher resistivity values. The strips were repeatedly washed in HCl to regenerate the resin, then measured in the respective HCl solutions. The regenerated resistivities returned, in most cases, to a value the same or approximating the original resistivity. All sample strips became stiffer and brittle at the highest acidity levels.

The CD1L-A5N behaved similarly to the above membranes (300 hours of exposure). The 103QZL-S (standard) showed a smaller increase in resistivity because of its highly porous resin structure which allowed greater intrusion of the more conductive H$^+$ and Cl$^-$ ions.

The cation membrane 61CZL exhibited the least overall increase in resistivity, however, the highest increase occured at the low acidity

range, contrary to the anion membrane behavior. This is due to the absorbtion of the cations Fe^{+3} and also $FeCl_2^{+1}$ and $FeCl^{+2}$ at low acidity and their removal at high acid levels by conversion to the negative complex ions.

Membrane resistivity is dependent on (i) the IEC, (ii) the mobility of the counter ion associated with the exchange site, and (iii) the mobility of the co-ions diffusing into the resin pore structure. The ionic species in $FeCl_3/HCl$ solutions include Fe^{+3}, H^+, Cl^- and the complex ions $FeCl_2^+$, $FeCl^{+2}$, $FeCl_4^-$, and $FeCl_6^{-3}$ at varying concentrations depending on the solution acidity. According to Dodson et al* in 3M HCl 0.44% of the Fe^{+3} ions are present in the negative complex form and increase to 98.1% at 6M HCl. Positive complex ions predominate at more dilute acidities.

At lower HCl concentrations where negative complex Fe^{+3} ions may be present in only trace amounts, the A3L-B7 and CP4L-A2N membranes required longer residence time in $FeCl_3$ to reach the resistivity region of 60-70 $\Omega-cm^2$. The anion membranes in the 0.5-1.0N HCl environment apparently acted as ion scavengers removing the trace amounts of negative complex ions as they formed until the resin sites were used up.

The above indicates that anion membranes are suceptible to large increases in resistance in a $FeCl_3$ environment of acidity 0.5N and higher.

Cation resin resistivity appears to be less adversely affected by $FeCl_3$, particularly at the higher acidity levels. A cation membrane synthesized for low porosity and low Fe^{+3} transfer was considered as an alternative to the candidate anion system, but failed structurally on testing in the Fe^{+3} transfer test cell.

*JACS 58, 2573 (1936)

5.0 PREPARATION OF CANDIDATE MEMBRANES

Approximately half way into the contract period, largely on the basis
of performance in NASA-LEWIS test cells, the two most promising candidate
formulations were selected for preparation in larger sizes and for detailed
evaluation of their 0.24 to 0.35 f_{NP} variations. The two systems selected
were the CD1L formulation   (vinylbenzylchloride-dimethylaminoethylmeth-
acrylate) and the CP4L formulation (vinylbenzylchloride-4-vinylpyridene).
In both of these systems the monomers react to form a quaternary adduct
between the VBC and the amine group before and during the polymerization
of the monomers. The quaternary adduct formation essentially results in
the high cross-link density of these polymers.

Typical structural representations of the copolymers are

CD1L

VBC
+
DMAEMA

and CP4L

VBC
+
4VP

$-(CH_2-CH-CH_2-CH)_n-$

$-(CH_2-CH_2)_n-$

$Cl^{\ominus}$

$Cl^{\ominus}$
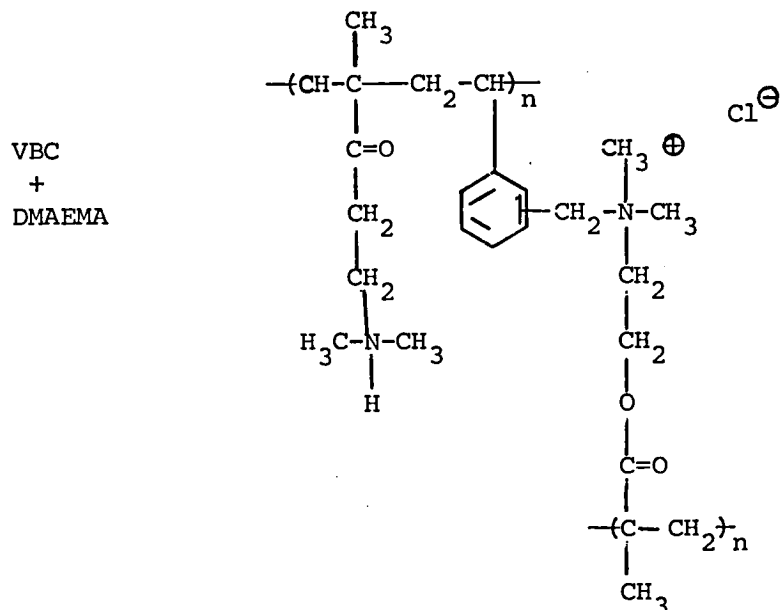
5.1 CP4L MEMBRANE PREPARATION

The CP4L-A2 type of membranes were prepared by the copolymerization of 4-vinylpyridine with vinylbenzylchloride in the presence of a non-reactive solvent. The formation of quarternary ammonium segments by the reaction of the VBC and the 4 VP proceeds at a fairly slow rate at room t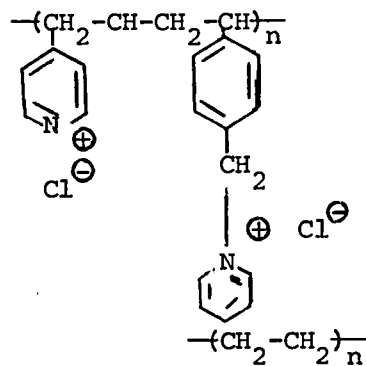emperature. This reaction causes only relatively limited increases in viscosity during the period of processing, the remainder of the reaction occurring during the polymerization cycle.

This membrane was selected as a prime candidate because it had low initial electrical resistivity and very low iron permeability as well as excellent chemical and mechanical stability in iron and chromium solutions to 80°C.

As a prime candidate a more detailed exploration of the systems performance was made in the .25 to .30 f_{NP} region. A series of membranes were fabricated at 0.25, 0.275 and 0.30 f_{NP}. These membranes were produced on a 22 mil modacrylic fabric and a thin modacrylic fabric, identified as CWH.

The resultant membranes were evaluated for ion exchange capacity, percent water, electrical resistance, and iron permeability. As usual these resins had very high ion exchange capacity and relatively low resistance particularly on the thinner fabrics.

Typical properties of the CP4L-A2 system at 25 NP were:

Ion Exchange Content	5.09 meq/gdr
Water Content	34%
Resistance (thin fabric)	2.8 Ω-cm^2 (1.0N HCl)
Permeability P_{Fe}^+ (thin fabric)	.008 mg/mF

Resistances on the 22 mil fabric were appreciably higher and iron permeabilities lower. The variations of f_{NP} studied showed iron permeability to increase moderately, on the thin fabric, from 0.25 to 0.275 and then sharply from 0.275 to 0.30 f_{NP}.

The variation in resistance with f_{NP} in this range was appreciable but not dramatic, dropping from about 2.8 Ω-cm^2 at 0.25 f_{NP} to 2.5 Ω-cm^2 at 0.30 f_{NP}. The results of tests on the CP4L-A2 systems at the various f_{NP}'s are given in Table VIII.

The low iron transfer and low initial resistance values in tests run at NASA-Lewis paralleled those run at Ionics. Additional tests by NASA-Lewis on the CP4L's resistance stability however indicated a high rate of increase of the membranes' resistance in an operational environment. For this reason the emphasis was shifted to CD1L A5 membranes.

SUMMARY CP4L-A2 Type Membranes

Advantages

Excellent selectivity - Low Permeability

Low initial resistivity

Excellent chemical durability

Easy to prepare

Disadvantages

Limited resistance stability.

T A B L E   V I I I

NONPOLYMER CONTENT VARIATIONS IN CP4L-A2 TYPE MEMBRANES

THIN FABRIC (CWH)

CP4L-A2 Type	25NP	27.5 NP	30NP
Resistance $\Omega\text{-cm}^2$ In 1.ON HCl (R_ℓ^J)	2.8	2.6	2.5
Thickness, centimeters	0.038	0.038	0.036
Permeability Fe^{+3} mg/mF $(X10^{-3})$	8	12	40
Water Content % Water	-	-	-

22 MIL FABRIC

	25NP	27.5 NP	30NP
Resistance $\Omega\text{-cm}^2$ In 0.1N HCl (Probe)	5.9	4.3	4.3
Thickness, centimeters	0.060	0.057	0.058
Water Content % Water	34.3	36.4	35.6
Ion Exchange Capacity Total (meq/gdr)	5.09	4.77	4.78
Strong	2.32	2.21	2.03
Weak	2.77	2.56	2.75

5.2 CD1L MEMBRANE PREPARATION

The CD1L-A5 type of membranes were prepared by the copolymerization

of dimethylaminoethylmethacrylate with vinylbenzylchloride in the

presence of a non reactive solvent. In this case the formation

of quaternary ammonium segments by reaction of the VBC and the DMAEMA,

after a short induction period, is fairly rapid even at room temperature.

This reaction causes a substantial viscosity increase and/or change in

wetting characteristics during the processing, the remainder of the

reaction occurring during the polymerization cycle.

This membrane was selected as a prime candidate because it had

relatively low initial electrical resistivity, and low iron permeability

as well as good chemical and mechanical stability in chromium and iron

solutions at room temperature.

A detailed study of this membrane systems' performance was made in

the 0.25 to 0.35 f_{NP} region. This N.P. range was selected as the 0.25 f_{NP}

lower limit had the desired low iron permeability (4 to 8 x 10^{-3} mg/MF)

and a reasonably low initial electrical resistance value. The higher f_{NP} region,

about 0.35, was chosen for the upper limit, as the iron permeability

of the membranes increased quite markedly at about 0.35 to 0.40. The

higher f_{NP} contents were included in the study as the resistance has

been noted to fall moderately as the f_{NP} is increased over this range.

A series of screening tests indicated this polymer system produced

membranes which increased in resistance in the test solutions, only at

a very slow rate. This membrane's good resistance stability was the

attribute that made it a prime candidate for the scale up to stack

tests.

Preparation of membranes in the 9" x 10" sizes and larger quantities

indicated some problems. The problems resulted in the production of

large numbers of membranes with leaks. One of the first studies was on the

viscosity of the system. The study indicated that rather large and

significant viscosity increases occurred during processing. These

increases were more pronounced the lower the N.P. content of the mix.

At 0.25 f_{NP} the viscosity of the solution would increase better than 2.5

times during a normal lay up procedure. Typically such increases at

$20^{o}C$ ran from 1.4 cps to 3.7 cps. It was concluded that this increase

in viscosity was due to the formation of an adduct of the VBC and

DMAEMA. Prompt processing schedules were instituted and resulted in

substantial improvements of the yield of leak free membranes. A typical

time vs. viscosity plot is presented in Figure   II. In this curve

the viscosity rises to a maximum of about 88 cps. This rise

probably indicates that the VBC-DMAEMA adduct forming reaction has been

completed. It appears unlikely that any substantial quantity of polymer

is formed during this reaction as the viscosity is still relatively

low for a concentrated solution of monomer -polymer such as this would be.

In the further study of the adduct monomer blend a three day old

mix of about 80 cps at $26^{o}C$ was heated slowly. The viscosity was monitored

during this heating and a 5 to 10 minute dwell time was observed after

each $5^{\circ}C$ rise. This test showed the viscosity to decrease till about

$45^{\circ}C$ (and about 100 minutes total heating time). Then from a low

of 32 cps the sample gelled rapidly (5-10 min). A plot of this data can

be seen in Figure III.

One of the most direct ways to decrease a membrane's resistance

has been to decrease its thickness. Generally, the decrease in resistance

will be roughly proportional to the thickness reduction if the weight

and cross section of the fabric backing decrease proportionally. In

this series the 22 mil fabric yielded membranes of 0.055 to 0.060 cm

in thickness. The thin modacrylic weaves yielded membranes about 0.035 to 0.040

cm thick. Another fabric investigated was a calendered modacrylic which

gave membranes of about 0.040 cm. Concurrently with the investigation

of the f_{NP} and fabric variations, studies were made to observe the

effect of various processing parameters on pinholes and leaks. Included

were

1. Presoaking of the fabrics in the VBC-DMAEMA-N.P. mix

2. Presoaking of the fabrics in the N.P. alone

3. Presoaking of the fabrics in the DMAEMA-N.P. mix

4. Effect of age of mix

5. Method of catalyst addition

6. Cure cycle variation

7. Space variation

8. Effect of f_{NP} variations

About 450 9" x 10" or larger CD1L membranes were made in this phase

of the program. After initial screening for leaks the most promising

were evaluated by testing for

     Burst strength

     Thickness

     Resistance (in HCl)

     Ion exchange capacity

     Water content

     Iron permeability.

These tests indicated that a number of the techniques produced

only minor improvements in the quality of the membranes. Leak free acceptable

membranes however were produced consistently only when the lay up

of membranes was completed rapidly, before the onset of the quarternization

of the monomers.

The effect of the processing variables on the properties of the

membranes were evaluated by leak and other tests. Table IX

compares the properties of membranes prepared in the regular manner with

those prepared with a presoak in monomer and non-polymerizable solvent.

The presoaks were run on both the 22 mil and thin modacrylic fabrics.

No dramatic or systematic changes in properties were noted.

Sets of 9" x 10" membranes were prepared on the thin cloth

at 0.25, 0.275, 0.30 and 0.35 f_{NP}. Another set on the 22 mil. cloth

was prepared for reference. Preliminary characterization tests on the thin

T A B L E   I X

EFFECT OF PRESOAK ON CD1L-A5 MEMBRANE PROPERTIES

Fabric:	22 Mil Modacrylic Standard			Modacrylic Thin		
Presoak	None	NP Solvent	Amine Monomer	None	NP Solvent	Amine Monomer
Thickness (cm)	0.065	--	--	0.035	--	--
Burst strength (psi)	--	126	133	--	91	96
R_ℓ^c Probe 0.1N HCl (ohms-cm^2)	5.9	4.0	4.0	3.9	5.4	4.7
Water Content (% water)	38.3	37.5	35.8	39.4	35.1	35.6
Ion Exchange Capacity (meq/gdr) Total	4.23	4.60	3.94	4.22	4.72	4.60
Strong	1.89	1.75	1.68	2.06	2.15	2.14
Weak	2.34	2.86	2.26	2.14	2.57	2.52

T A B L E X

COMPARISON OF CALENDERED FABRIC WITH REGULAR FABRIC

CD1L-A5	CALENDERED			
	25NP	27.5NP	30NP	33.3NP
Resistance(Ω-cm^2)				
In 0.1N HCl	4.6	4.6	4.5	--
In 1.0N HCl	3.33	3.64	3.67	2.93
Thickness(cm)	0.035	0.037	0.040	--
P^+_{Fe} (mg/mG x 10^{-3})	5-8	2-7	6-10	6-13
Water Content (% Water)	33.9	35.7	37.0	--
Ion Exchange Capacity				
Total (meq/gdr)	4.28	4.36	4.02	
Strong	2.08	2.01	2.03	
Weak	2.20	2.35	1.99	

	REGULAR (22 MIL MODACRYLIC FABRIC)			
	25NP	27.5NP	30NP	33.3NP
Resistance (Ω-cm^2)	4.42	--	3.94	3.36
P^+_{Fe} (mg/mF x 10^{-3})	2-4	--	2-5	---

fabric indicated their iron permeability was marginal. Further tests

at NASA-LEWIS showed the iron permeability of the thin membranes

was too high and increased emphasis was put on the utilization of

the calendered modacrylic fabric.

Membranes prepared on the calendered fabric were generally thinner

(0.040 cm) and appeared good. Sets of six membranes (11" x 12") were

prepared on this fabric at f_{NP}'s of 0.25, 0.275, 0.30 and 0.33. These

membranes along with one each of a set of controls on 22 mil modacrylic

(at 0.25, 0.30 and 0.35 f_{NP}) were characterized in detail, Table X.

The resistance values on the calendered fabric ran about .3 to 1.1 $\Omega\text{-cm}^2$

lower than their counterpart on the 22 mil modacrylic fabric. The

iron permeability measurements were quite good and stayed below

10×10^{-3} mg/mF up to the f_{NP} = 0.30 level.

The NASA-LEWIS schedule for construction of some trial stacks made

it necessary at this point to begin to fabricate 25 membranes in the 11"

x 12" size. The CD1L-A5 on calendered modacrylic fabric was selected

as the best choice at this point the the program. The membranes

were fabricated in three lots. The individual lots were characterized

by resistance, thickness, ion exchange capacity, and water content.

The results of these tests are tabulated in Table XI.

Subsequently ten more CD1L A5 11" x 12" membranes were fabricated for

the same use. This lot was also characterized and the results of these

tests are included in Table XI as Lot AS-21.

T A B L E   X I

MEMBRANE PROPERTY COMPARISON

Four Lots - 10" x 11" Size

CALENDERED FABRIC

CD1L-A5 Lot	AS16	AS17	AS18	AS21
Resistance(Ω-cm^2) In 0.1N HCl	5.6	5.3	5.3	5.4
Thickness (cm)	0.044	0.044	0.046	0.047
Water Content (% Water)	32.5	35.3	33.1	33.3
Ion Exchange Capacities (meq/gdr) Total	4.19	4.34	4.13	4.20
Strong	2.13	2.17	2.14	1.70
Weak	2.06	2.17	1.99	2.50

Preparation of the CD1L-A5 membranes at the lower f_{NP} requires considerable care and expertise. Even with the best techniques yet developed, the yield of leak free membranes in the 0.25 to 0.30 f_{NP} is about 60 to 80%. However no longer are failures so massive as in the early membranes; now they are more apt to be a single pinhole or a minor leak.

Because of these difficulties several attempts to use different non-polymerizing solvents as N.P.'s were made, however yields were lower than with the usual solvent.

Evaluation Summary CD1L-A5 membranes

    Advantages - Good to excellent selectivitity- Low permeability

            - Low initial resistivity

            - Excellent chemical and mechanical durability at room temperature

            - Fabrication with reasonable ease

    Disadvantages - Chemical and mechanical durability at elevated temperatures in chromium ion solutions may be marginal.

6.0 BROMINATION OF MEMBRANES

Some previous work had shown that the treatment of certain membranes with bromine solutions yielded membranes with improved electrical resistance stability due, apparently, to improved antifouling properties. This treatment reduced the membrane permeability to iron but increased its initial electrical resistance somewhat.

Two CD1L series membranes, one having 0.35 and the other 0.40 f_{NP}, were treated with bromine solutions. Subsequent dye testing indicated gross leakage of the membranes. The results of one set of these tests is tabulated below:

BROMINE TREATED MEMBRANES

CD1L-A5P
(f_{NP} = 0.40)

REGULAR FABRIC

	Bromine Treatment	Resistance* (Ω-cm^2)	P_{Fe}^{+} (mg/mF)	Leak Test**
Control	None	2.20	0.15 to 0.25	OK
Sample #1	24 Hours	2.69	34.6	Massive
Sample #2	120 Hours	2.81	--	Massive

* in 1N HCl
**due penetration

In view of the negative results with these CD1L membranes it was decided to suspend further effort on this treatment until a reevaluation of the process could be made.

7.0 IRON PERMEABILITY TEST CELL

A new iron permeability test cell was fabricated during the contract period. The old test cell had become marginal in operation. Some minor cracks and checks had been noted in the methylmethacrylate plates that were used to make up the compartments of the cell.

The design of the new cell was similar to the old except the size of the chambers holding the iron solutions and the hydrochloric acid were enlarged. The enlarged area was about 3.7 cm x 1.5 cm. The current density was maintained at 60 ma/cm^2. The new cell incorporated another change. It used anion membranes throughout to prevent iron from flowing into the H_2SO_4 solution surrounding the anolytes and catholytes. A sketch of the test apparatus may be found in Figure IV.

GLOSSARY

VBC - Vinylbenzylchloride

DMAEMA - Dimethylaminoethylmethacrylate

4-VP - 4-Vinylpyridine

2-VP - 2-Vinylpyridine

CD1L - Candidate Membrane System - Copolymer of VBC and DMAEMA

A3L - Candidate Membrane System - Copolymer of 2-VP and DVB

R_ℓ^J - Area resistance by liquid junction method $(ohm\text{-}cm^2)$

R_ℓ^C - Area resistance by contact probe method $(ohm\text{-}cm^2)$

P_{Fe}^+ - Permeation factor for Fe in the charging mode $(mg\ Fe/mF)$

mF - millifaraday $(96.5 \times 10^3\ ma\text{-}sec)$

IEC - Ion exchange capacity   (meq/gram dry resin)
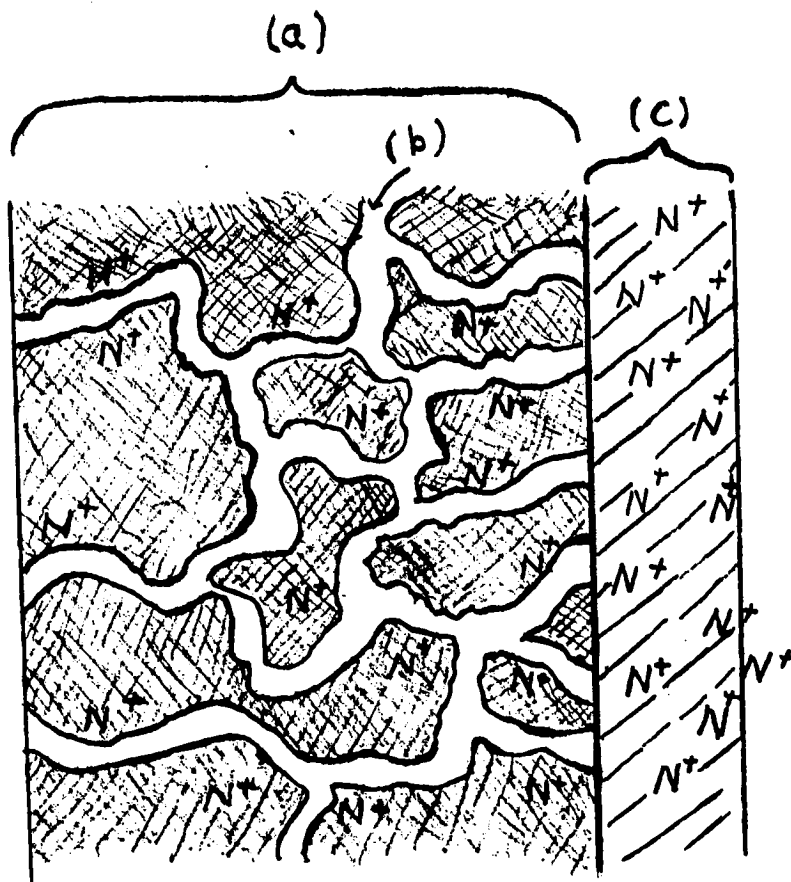
F I G U R E I

COMPOSITE MEMBRANE STRUCTURE: SCHEMATIC

(a)   Porous Substrate

(b)   Substrate Pores

(c)   Dense Film of Anion Selective Resin

(N^+) Amino Ion Exchange Site

F I G U R E   I I

QUATERNARY FORMATION

Time versus Viscosity

CD1L-A5 f_{NP} 0.25
Cup Temp. 24°C

VISCOSITY (cps) vs TIME (min)

FIGURE III

HEATING OF ADDUCT BLEND

Temperature/Viscosity/Time Plot
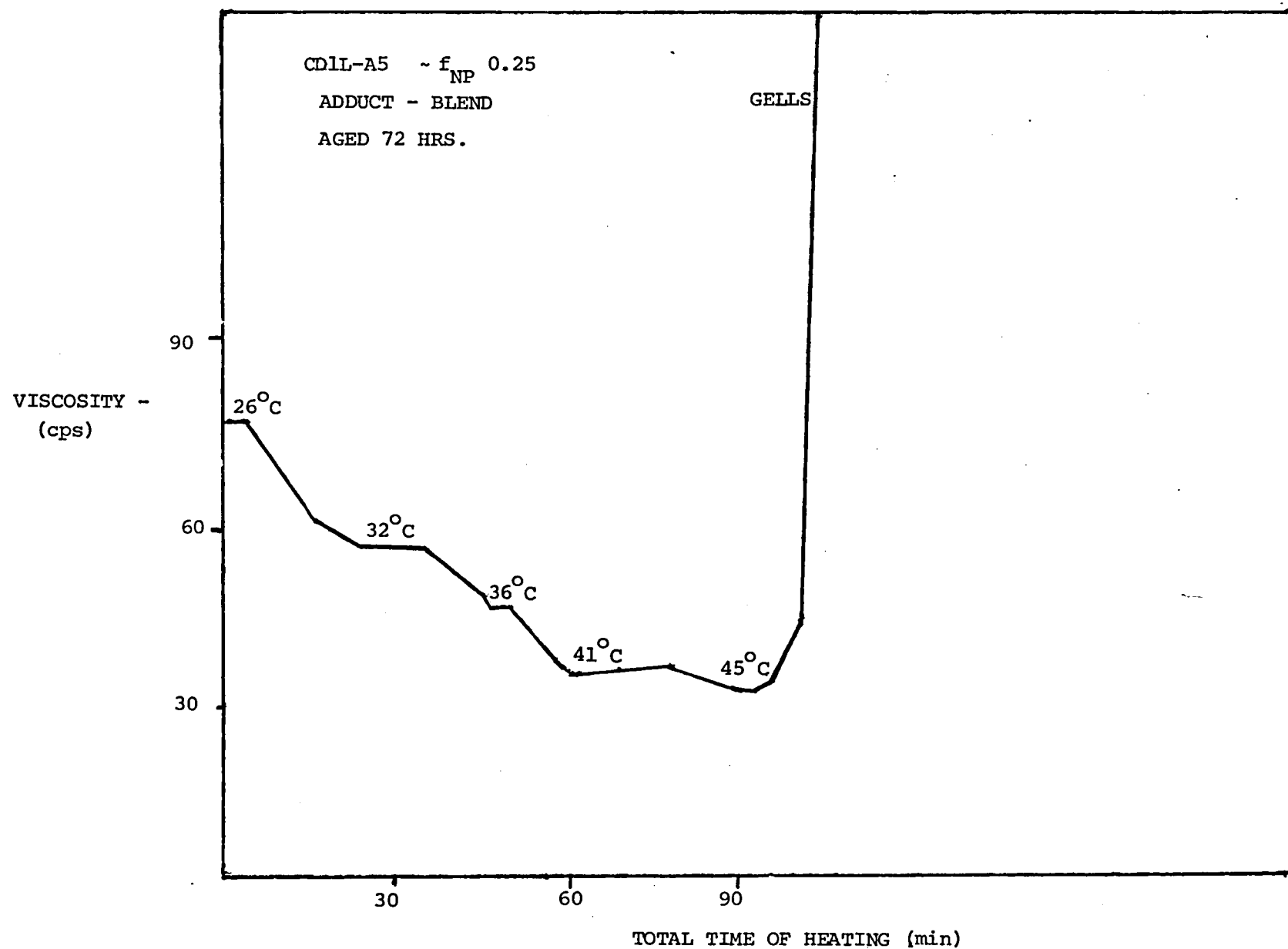
FIGURE IV

IRON PERMEABILITY

Membrane Test Cell - Lucite

Plastic End Block

Platinum (Negative) Electrode

Sulfuric Acid Chamber

Anion Membrane

HCl Chamber

Test
Membrane

$FeCl_3$ Chamber

Anion Membrane

H_2SO_4 Chamber

Platinum
(Pos.) Elect.

Plastic
End
Block
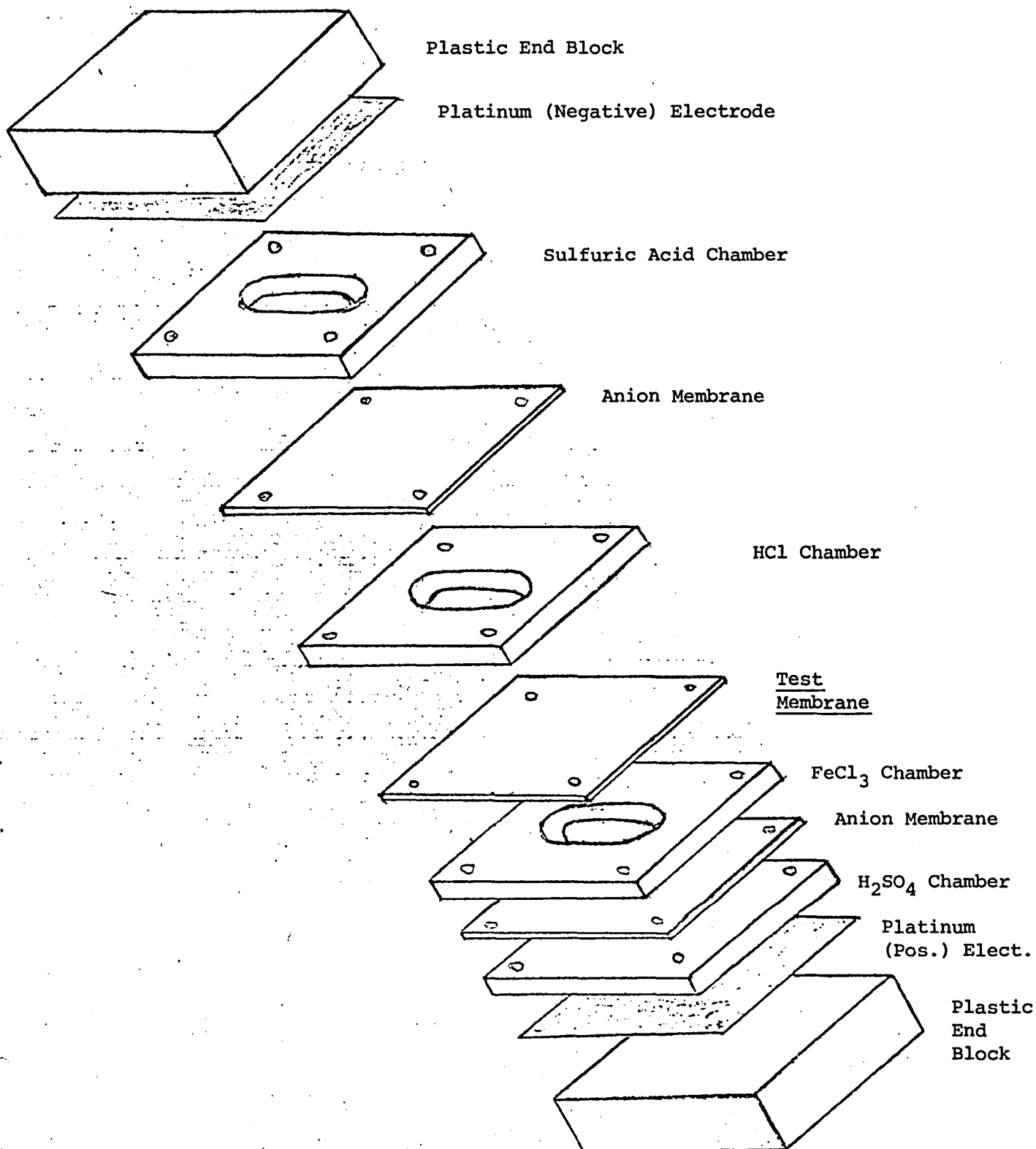
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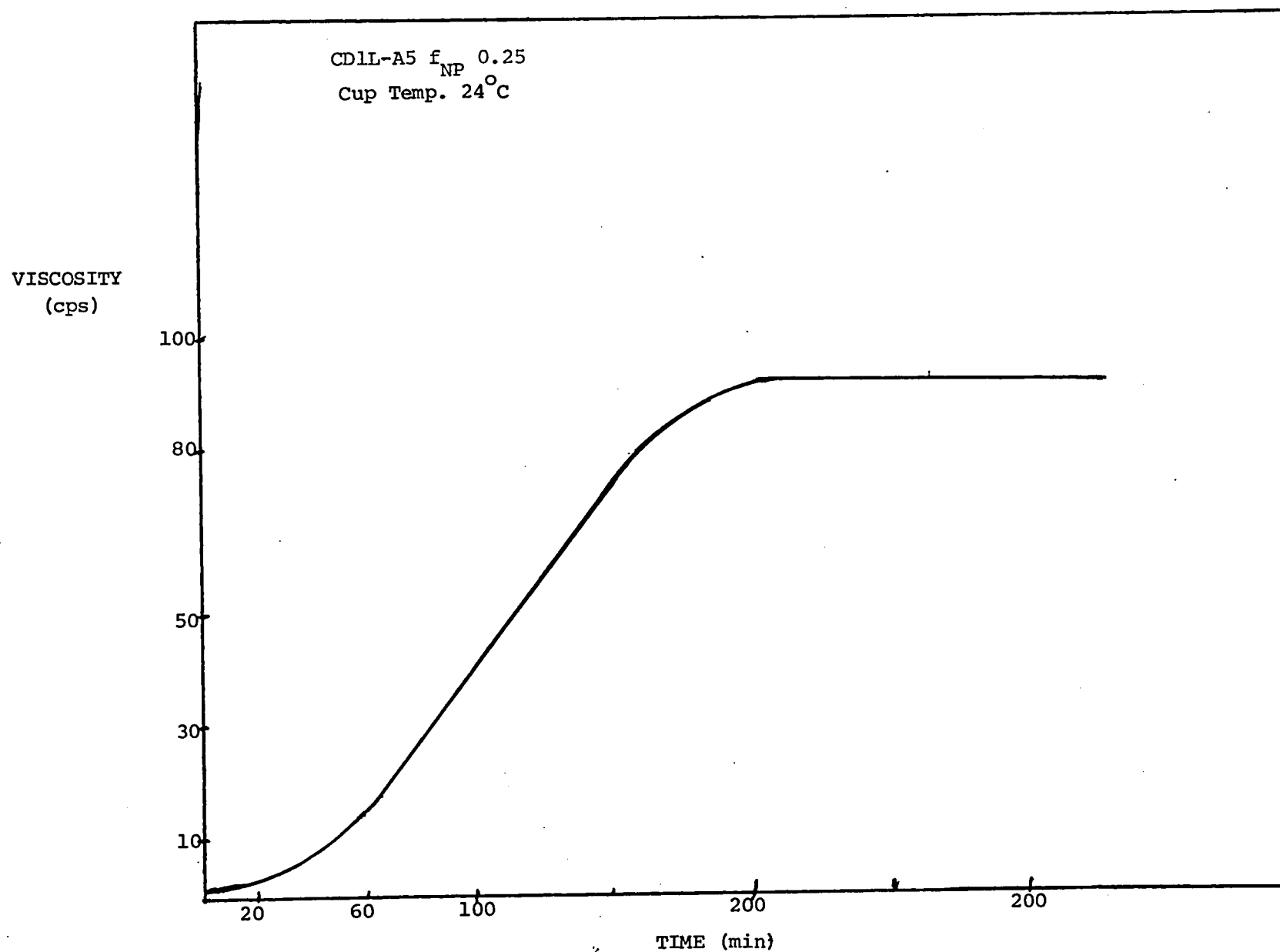|	
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15. Supplementary Notes

    Prepared under Interagency Agreement #(49-28)-1002
    Project Manager: Richard W. Lauver
                       NASA Lewis Research Center
                       Cleveland, Ohio 44135

16. Abstract Experimental composite membranes were synthesized on a lab scale consisting of a thin layer of anion permselective resin supported by and bonded to a porous physically strong and conductive substrate film. These showed good selectivity and also substantially lower electrical resistivities than the homogenous candidate membranes optimized in the previous contract.

    A wide range of resin porosities were examined for three candidate membrane systems, CD1L, CP4L, and A3L to identify the formulation giving the best overall redox cell performance. The objective was to obtain the optimum membrane porosity giving an acceptable selectivity and long range resistance stability in redox cell operation.

    Candidate anion membranes showed large increases in resistivity after a short time of immersion in concentrated $FeCl_3$/HCl solution. The resistance rise was attributed to exchange site fouling by the complex ions $FeCl_4^{-1}$ and $FeCl_6^{-3}$ and was found to be reversible by HCl washing.

    Limited quantities of two candidate membranes CD1L and CP4L (in the 10" x 10" size) were made up using several fabrics and various N.P. contents from 25 to 33%. Largely on the basis of resistance stability the CD1L formulation was selected as prime candidate and about thrity-five membranes (one foot square) were produced for experimental static and dynamic evaluation.

    A better appreciation of the significance of the various processing parameters was gained during this study. This improved understanding permitted us to increase the batch size and therefore the number of membranes per batch, while making substantial improvements in both uniformity and reliability.

17. Key Words (Suggested by Author(s))
Semipermeable membrane, Permselective membrane, Anion membrane, Electrochemistry, Separator, Electrical Storage, Redox
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