ANION PERMSELECTIVE MEMBRANE

by

Samuel S. Alexander
Russell B. Hodgdon

Ionics, Incorporated
Research Division
65 Grove Street
Watertown, Massachusetts 02172

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS 3-20108

Richard W. Lauver, Project Manager
To: NASA-Lewis Research Center  
Cleveland, Ohio 44135  
Attn: Mr. R. W. Lauver  
301-2; MS 49-1

A Summary Report  
Anion Permselective Membrane  
NAS 3-20108

Submitted by: Research Division  
Ionics, Incorporated  
65 Grove Street  
Watertown, Massachusetts 02172  
Tel: (617) 926-2500

Prepared by: Samuel S. Alexander  
Russell B. Hodgdon

Approved: 

Edgardo J. Parsi  
Director of Research
FORWARD

This document constitutes the final report for the work accomplished between June 1975 and July 1977 by Ionics, Incorporated for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS-3-20108 entitled SYNTHESIS AND CHARACTERIZATION OF IMPROVED ION SELECTIVE SEMIPERMEABLE ANION EXCHANGE MEMBRANES.

Dr. Russell B. Hodgdon provided overall program management. The principal investigator was Samuel S. Alexander with major contribution from W. W. Saite, C. H. Swenson, A. Scieszko and R. B. Hodgdon.

Thanks are due to Cindi Krawczyk for her patience in typing the final report manuscript and its many revisions.
1.0 **INTRODUCTION AND SUMMARY**

The objective of NAS 3-20108 was the development and evaluation of improved anion selective membranes useful as efficient separators in a redox power storage cell system being constructed at the NASA Lewis Research Center, Cleveland.

The program was divided into three parts, (a) optimization of the selected candidate membrane systems, (b) investigation of alternative membrane/polymer systems, and (c) characterization of candidate membranes. The major synthesis effort was aimed at improving and optimizing as far as possible each candidate system with respect to three critical membrane properties essential for good redox cell performance.

1. high selectivity, minimal transfer of the reactive metal cations (Contract target - $10^{-4}$ equivalents Fe$^{+3}$ per Faraday or less)

2. low electrical resistivity (Contract target - 20 ohm-cm or less in 1M HCl at 80°C)

3. long term durability in redox environments (Contract target - at least 1000 hours in 2M FeCl$_3$ and 2M CrCl$_3$ at 80°C).

Substantial improvements were made in 5 candidate membrane systems, the 103QZL, A3L, B2LDT, C6L and CP4L. These were prepared by the bulk polymerization of liquid monomers on synthetic fabric backing. The critical synthesis variables of cross-link density, monomer ratio, and solvent composition were examined over a wide range. A sixth system was included in the candidate group, the A3L-96, in a low porosity configuration.

In addition, eight alternative polymer systems were investigated, two of which, the CD1L and CP4L, attained candidate status. Three other alternatives showed potential but required further research and development. These were the VC-TP (aminated PVC film), CT and CTM systems.

Each candidate system was optimized for selectivity. In each case the optimum monomer formulations were identified which produced membranes
with a minimal transfer rate for Fe$^{+3}$. In general, these were formulations having the minimum solvent content which could yield physically stable membranes. The best membranes of the candidate group gave transfers of $1-8 \times 10^{-3}$ mg Fe/mF, a range which approaches the contract target transfer rate of $10^{-4}$ equivalents per Faraday. Analogous candidate membranes which were synthesized in the previous contract period had yielded transfer rates of $50-1000 \times 10^{-3}$ mg Fe/mF.

The specific resistivities of the optimized candidate resins were about 35-65 ohm-cm in 1N HCl at 80°C. Improvement in the absolute electric resistance of the membranes was demonstrated by reducing the film thickness below that of the standard Dynel backed membranes (0.6 mm). The membrane resistance was reduced by a factor of about two to three by the use of a variety of light weight fabrics as backing material. These included material in modacrylic, Teflon™, polypropylene and glass. The most successful light weight fabric was a woven modacrylic yielding the lowest resistivity ($2\pi$-cm$^2$) and excellent durability in the CP4L membrane system. This fabric, however, was compatible only in the more polar monomer systems (the CP4L and the CDIL). Other materials showed variable results. Only the membranes on the standard Dynel woven and the above modacrylic have shown the most consistence and reliable physical integrity on manufacture; and long term durability on testing. A film thickness of about .10-.25 mm appears to be the minimum feasible range for viable membrane manufactured by bulk polymerization and fabric saturation.

Very low resistivities were measured in the VC-TP system (aminated thin commercial PVC film) but candidate status was not recommended because of excessive Fe$^{+3}$ permeability and IEC loss at elevated temperature.

The candidate ranking highest in overall properties and performance
was the CP4L-A2 membrane, a copolymer of 4 vinylpyridine and vinylbenzyl-chloride. The optimized CP4L-A2 membrane (on woven modacrylic) was a rugged, extremely durable film 0.23 mm in thickness with an area resistivity $R^c = 1.8 \, \text{ohm-cm}^2$, and permeability, $p^{+}_{\text{Fe}} = 4-8 \times 10^{-3} \, \text{mg Fe/mF}$. The total IEC was about 5 meq/dgr. (50% strong base), the highest in the candidate group. The stability of all critical membrane properties was excellent after 1000 hours in both 2M FeCl$_3$ and 2M CrCl$_3$ at 80°C. (Table 1).

The other candidate membranes ranked below the CP4L system because of one or more deficits and are listed below in the descending order of overall desirable properties.

The A3L-B7 membrane - a copolymer of 2 vinylpyridine and divinyl-benzene ranked next in overall desirable properties. It was successfully manufactured on a production scale in 5.5 ft$^2$ area sheets on Dynel woven fabric. The membrane had excellent durability in both electrolyte solutions at 80°C and very low permeability to Fe$^{3+}$. Substantial improvement in resin durability was obtained by the use of DVB in place of ethylene glycol dimethacrylate, the cross linker used in the earlier syntheses. The resistivity of the A3L-B7, however, was at the high end of the candidate range. Membrane samples on woven Teflon and other lightweight backings were made on a lab scale showing 50% or more improvement in area resistivity, but were variable with respect to film integrity.

The 103QZL-B10 membrane - a copolymer of DVB and VBC post aminated with trimethylamine was optimized for selectivity giving a transfer rate of $2 - 3 \times 10^{-3} \, \text{mg Fe/mF}$. The minimal absolute resistivity was obtained on Teflon backing which yielded a membrane film 0.27 mm in thickness and a corresponding decrease of about 50% resistance. Resin durability was excellent in FeCl$_3$ at 80°C but only fair in CrCl$_3$ and 80°C, showing some loss of selectivity in the latter electrolyte. At present, large
scale manufacture is feasible only on woven Dynel.

The CD1L-A5 and A5H membranes are copolymers of VBC and dimethylamino-ethyl methacrylate (DMAEMA). The membranes have a high IEC of 4.5 meq/dgr and a low resistivity, $R_\Omega$, of 2.9 ohm-cm$^2$.

The membrane, 0.11 mm in thickness, was successfully prepared in lab scale on light weight modacrylic fabric which represented the minimum film gage and resistivity in this system. Thin membrane durability was excellent in FeCl$_3$ at 80$^\circ$C and in CrCl$_3$ only at ambient temperature. The minimum transfer rate was $4.8 \times 10^{-3}$ mg Fe/mF.

The B2LDT-B2 membrane, a copolymer of VBC and DVB post aminated with diethylenetriamine (DETA), showed extremely stable resin properties in both electrolytes at 80$^\circ$C but only fair to poor durability for the membranes on woven Dynel and Teflon respectively. This was attributed to fabric damage of the Dynel in manufacture and inadequate resin fiber adhesion for the Teflon. The minimum membrane gage obtained was 0.27 mm on woven Teflon yielding the minimal resistivity for this system $R_\Omega = 4.1$ ohm-cm$^2$. The optimized transfer rate was $1 - 2 \times 10^{-3}$ mg Fe/mF.

The A3L-96 membrane - a copolymer of 2VP and ethylene glycol dimethacrylate (EGDM) had shown good durability in the previous program but only at ambient temperature. This membrane system was chosen as the sixth candidate because of the ease of manufacture in a one step polymerization, and potentially low transfer rate.

The alternative systems VC-TP, CT, and CTM were found promising but requiring more R & D to create viable films.

The VC-TP membrane system - PVC film aminated with tetraethylene-pentamine (TEPA) - showed promise because of its relatively high porosity, high conductivity, and physical strength at .050 .20 mm thickness.
The CT polymer system - a copolymer of VBC and TEPA gave an unusually high IEC in the region of 6-7 meq/dgr. Higher cross linking was indicated for the production of a stable film structure.

The CTM polymer system - a copolymer of VBC and N, N, N', N' tetramethylethylenediamine (TMEDA) yielded a high IEC of 4.5 meq/dgr which was over 90% in strong base capacity. Higher cross linking was also indicated here to effect a more stable resin structure.

Characterization of the membranes was not completed, but sufficient data were obtained to rank candidates in order of their probable usefulness in the redox system. The resistivity of the optimized candidates over a wide range of HCl and NaCl concentrations was found to be a good measure of the candidate's relative effectiveness in excluding the cations H⁺ and Na⁺. The most effective candidate membrane CD1L-A5 and CP4L-A2 showed the least resistivity change over the entire concentration range.

The Fe³⁺ transfer rate, \( P_{Fe}^{+} \), was measured for four candidate membranes as a function of FeCl₃ concentration over a range of 0.5 to 4.0 N. The transfer rate was constant or slightly increased in the 0.5 - 2.0 N span but increased sharply by a factor of approximately three for the more selective membranes at 4.0N FeCl₃. The transfer rate of the most porous membranes of the series, the 103QZL-B2, increased by a factor of 8.

Polarization effects were indicated by the extremely low Fe transfer rates in high porosity membranes on application of high current densities. The 103QZL19S membrane gave a \( P_{Fe}^{+} \) of about 1-4 mg Fe/mF at 15-120 ma/cm² range and decreased by 500% to 9 x 10⁻³ mg Fe/mF at 480 ma/cm². Low porosity selective candidate membranes showed little or no variable transfer effects over the same range.
2.0 MEMBRANE SYNTHESIS - CANDIDATE SYSTEMS

In Task II (NAS 3-20108) five candidate membrane/polymer systems were investigated with the aim of optimizing the critical membrane properties of selectivity, resistivity, and durability. Three candidates were selected from the previous contract effort; systems 103QZL, A3L, and B2LDT; and two membranes reached candidate status out of Task I of the present contract, systems CD1L and CP4L. A sixth candidate was included, the A3L-96 membrane in a low porosity configuration.

The membranes were prepared using the bulk polymerization method with monomer saturation of the fabric backing. A wide range of the major synthesis variables were studied and related to the physical quality, integrity of the polymer film and various electrochemical properties of the membrane. The major synthesis variables were (1) cross-link density \( f_{XL} \) or molar ratio of the co-monomers \( \beta \), and (2) non-polymer solvent fraction \( f_{NP} \).

Each membrane system was optimized at a sheet thickness of 0.60 mm using woven Dynel fabric as the film backing material because of its superior system compatibility and durability. Scale up to production size film, 5.5 ft\(^2\) in area per sheet, was judged to be feasible for all the candidate systems and was demonstrated for two, the 103QZL-B2 and A3L-B7 membranes. These membranes were manufactured on a production scale, in good yield with uniform physical and chemical properties.

Improvement in resistivity was achieved by reduction of the membrane thickness through the use of light weight synthetic fabric backing. Membranes were produced on a lab scale in the 0.12-0.25 mm thickness range and showed a corresponding, but not linear decrease in area resistivity. Manufacturing procedures for fabricating acceptable thin membranes on a large scale were not fully established. Further investigation will be needed in this area. (Table 1).
2.1 THE 103QZL SYSTEM

The 103QZL candidate membranes are copolymers of vinylbenzylchloride (VBC) and divinylbenzene (DVB) post reacted with trimethylamine (TMA). The polymer network consists of a vinyl backbone crosslinked by DVB and contains a pendant strong base ion exchange group, benzyl trimethylammonium chloride (Figure 1a).

The membranes are prepared in a two step process (a) polymerization of the film and (b) amination to affix the quaternary ammonium chloride groups.

A series of 103QZL type membranes were prepared from different formulations representing a wide range of monomer and non-polymerizable solvent compositions. The membrane 103QZL-B10 was found to yield the maximum selectivity in this series together with good physical and chemical properties (Table 2). The optimum monomer formulation, designated as B10, consisted of a nominal crosslink density, \( f_{XL} = 0.35 \), and a non-polymer solvent content, \( f_{NP} = 0.30 \). The crosslink agent was DVB.

The optimized membrane 103QZL-B10 as manufactured on woven Dynel backing was a strong flexible anion selective membrane sheet 0.60 mm in thickness and had the following properties:

- IEC = 2.24 meq/dgr
- \( H_2O \) content = 25.4%
- Area Resistivity, \( R^C \), in 0.1N HCl = 10.6 \( \Omega \)-cm
- \( Fe^{+3} \) transfer, \( P_{Fe}^+ = 2-3 \times 10^{-3} \) mg Fe/mF

The B10 membrane on Dynel fabric was produced in good yield in 1 ft\(^2\) sections and could be manufactured in sheets 5.5 ft\(^2\) in area (50 x 100 cm).

The Dynel backed B10 showed excellent durability in 2M FeCl\(_3\) at 80°C. The durability in 2M CrCl\(_3\) was expected to be similar to that obtained in the case of 103QZL-B2 membranes. Loss of selectivity was measured after 100 hrs but remained essentially constant from the 200 hr. to the 1000 hr. point.
The B-10 membrane was also prepared on a lab scale on woven Teflon fabric which reduced the membrane thickness to 0.25 mm resulting in a corresponding decrease in area resistivity, \( R_{\text{c}} = 5.5 \ \Omega \cdot \text{cm}^2 \). (Table 1). The Teflon fabric has not yet proven to be a satisfactory improvement over Dynel due to the prevalence of pinhole defects in the Teflon backed membranes as manufactured.

The modacrylic fabric was not usable in the 103QZL system because of its partial solubility in the hot monomer solution. None of the polypropylene non-wovens produced films of any useful quality.

Further improvement in membrane resistivity requires creation of thin continuous membrane films on light weight fabrics or substrates which are both chemically compatible with monomeric constituents and resistive to the redox environment.

A summary of the experimental monomer formulations tested is given in Table 2. The major synthesis variables were; (1) crosslink density \( f_{\text{XL}} \) and (2) non-polymer solvent content \( f_{\text{NP}} \).

\( f_{\text{XL}} \) has been defined as the mole fraction of the crosslink monomer based on the total monomer present.

**Evaluation Summary - 103 QZL-B10 Membrane**

- B-10 formulation optimum for selectivity.
- Large scale manufacture feasible on Dynel woven fabric.
- Membrane on Dynel woven backing is rugged, flexible and durable in redox environment at 80°C.
- Improvement in resistivity achieved on lab scale by film gage reduction.
- More R & D needed on backings and substrates in order to improve quality.
2.2 THE A3L SYSTEM

The A3L membrane/polymer system is a copolymer of 2 vinyl pyridine (2VP) and DVB. The membranes are formed in a one step process by the polymerization of the monomers and solvent on fabric by means of heat and an initiator. The tertiary cyclic amino group is introduced directly into the polymer structure by the 2 VP monomer and no chemical post treatment is needed to activate the resin. (Figure 1b)

A series of A3L membranes were prepared on lab scale with varying proportions of monomers and solvent using Ven Dynel fabric as backing material. The optimized membrane in this group was the A3L-B7 membrane yielding the lowest Fe$^{3+}$ transfer value together with good physical and chemical properties. The A3L-B7 polymer was crosslinked with DVB.

The optimum monomer formulation for B-7 consisted of a crosslink density, $f_{XL}$ of .30 and a solvent content, $f_{NP}$, of .25. (Table 4)

The A3L-B7 membrane was manufactured in production size sheets, 5.5 ft$^2$ in area at .60 mm thickness with uniform physical and chemical properties. These were:

IEC = 3.2-3.8 meq/dgr

H$_2$O Content = 30.8-33.5%

Area Resistivity, $R^0$ in 0.1N HCl = 9.1-10.3 kΩ-cm$^2$

Fe Transfer, $P_{Fe}^{+}$ = 1-2x$10^{-3}$ mg Fe/mF

As predicted, DVB monomer imparted superior chemical stability (in 2M FeCl$_3$ and 2M CrCl$_3$ at 80°C) to the A3L membrane/polymer system in contrast to the A3L membranes of the previous contract period which used ethylene glycol dimethacrylate (EGDM) as the crosslink agent. The optimized A3L-B7 membrane showed excellent durability in both FeCl$_3$ and CrCl$_3$ solutions at 80°C for 1000 hr exposure time. (Table 12). The A3L membranes containing EGDM deteriorated progressively under the same conditions.

It was demonstrated that the membrane area resistivity could be
substantially improved by the use of light weight synthetic backings of substrates in place of the standard candidate backing, woven Dynel (Table 5). The choice of a backing material is limited by both its compatibility with the resin system and its chemical resistance to the redox environment. At this time, woven Dynel remains the best all around backing material for the A3L system polymers. The fabrics which produced coherent samples on lab scale were woven Teflon and non-woven polypropylene. However, the quality and durability on standing were variable and none achieved the overall reliability of the Dynel.

Evaluation Summary - A3L-B7 Membrane

-B7 formulation optimum for selectivity.

-Large scale manufacture successfully demonstrated on dynel woven fabric.

-Membrane is rugged, flexible and has excellent durability in redox environment at 80°C.

-Resistivity improvement by decrease in film/fabric thickness demonstrated on lab scale.

-More R & D needed to improve film quality of thin membranes.
2.3 THE B2LDT SYSTEM

The B2LDT membrane comprises the same basic polymer structure as the 103QZL but is aminated with diethylene triamine (DETA) to form mainly primary and secondary amino groups (Figure 1c).

The polymer film is formed in the identical manner as the 103QZL by the polymerization of VBC and DVB in solvent on synthetic fabric backing by means of heat and an initiator.

The optimum membrane in this system was the B2LDT-B2 which showed the lowest Fe transfer value and acceptable physical and chemical properties (Table 6).

The base polymer film has been manufactured successfully in large size sheets 5.5 ft\(^2\) in area on woven Dynel fabric. The B2LDT-B2 polymer structure and ion exchange groups showed excellent long range stability in both FeCl\(_3\) and CrCl\(_3\) solutions at 80\(^\circ\)C. (Table 12)

However, the unsatisfactory durability results reported on the B2LDT-B2 membranes were related to the failure of the supporting fabric. In the case of the woven Dynel, the fabric was damaged and weakened during the amination process leading to further physical deterioration of the film and transfer properties during the long range durability test.

The B2LDT-B2 on woven Teflon showed increased Fe\(^{3+}\) transfer and eventual cross leakage in the 1000 hr durability test indicating insufficient resin fiber bonding.

The properties of the optimized B2LDT-B2 membrane on Dynel fabric were:

IEC = 3.5 meq/dgr

Water Content = 29.9%

Area Resistivity, \(R_C^\phi\), in 0.1N HCl = \(8.7 \, \Omega\cdot\text{cm}^2\)

Fe transfer, \(P_{Fe}^+ = 1-2 \times 10^{-3} \, \text{mg Fe/mF}\)

Improvement in area resistance by fiber gage reduction was achieved on woven Teflon (\(R_C^\phi = 4.1 \, \Omega\cdot\text{cm}^2\)). Woven MoCacrylic proved unsuitable
because of its solubility in the monomer solution.

Thin film B2LDT-B2 membranes require further research and development on woven and non-woven support fabrics.

### Evaluation Summary - B2LDT-B2 Membrane

- Selectivity optimized at target value or better for Fe transfer.
- Large scale manufacture feasible on woven Dynel fabric.
- Polymer and exchange groups show excellent stability in redox environment at 80°C.
- Use and treatment of support fabric and substrates requires more R & D.
2.4 THE CDL SYSTEM

The CDL membrane is a copolymer of vinylbenzyl chloride (VBC) and
dimethylaminoethyl methacrylate (DMAEMA) in which the cross links are
formed by the condensation reaction of the benzylchloride group of VBC
and the tertiary amino group of DMAEMA. (Figure 1d)

The CDL membrane can be prepared by either a one step or two step
synthesis.

(1) One Step Synthesis - The backing fabric is first saturated
with a homogenous solution of the monomers and an initiator in solvent.
The membrane sheet is then formed between glass plates in a single heating
operation by the simultaneous in situ polymerization of the vinyl groups
and condensation of the amino and vinyl benzyl groups to form quaternary
ammonium chloride sites.

(2) Two Step Synthesis - VBC and DMAEMA are first reacted in H₂O
to form a water soluble condensation product, a quaternary ammonium
chloride salt of VBC and DMAEMA. Initiator is dissolved and the
membrane sheet is formed in a second heating operation by the polymeriza-
tion of the vinyl groups.

The optimum membrane selectivity in the CDL system measured by
minimal Fe⁺³ transfer (F⁺³Fe) was most closely related, as in other systems,
to the solvent fraction (FNP) used. The membranes CDL A5, A5H, A6 and
A6H yielded the minimal P⁺Fe value and were prepared with the lowest solvent
fraction in the series tested. (Table 7)

The membranes CDL-A5 and A5H were selected for candidate status
because of their apparent lower resistivity.

The membrane thickness was reduced to 0.11 mm from the standard of
0.60 mm by the successful use of light weight woven modacrylic. However,
the apparent improvement was only a 50% decrease or less in area resistivity
R²Fe. This may be due to the more dense yarn construction of the thinner
cloth.

Lab scale samples with good physical quality were prepared on woven
modacrylic using the one step synthesis. Scale up to production size was
not attempted.
The optimized CDLL-A5 on modacrylic fabric had the following properties:

IEC = 4.02 meq/dgr (-50% in strong base capacity)

$H_2O$ Content = 30.1%

Area Resistivity, $R^C$, in 0.1N HCl = 2.9 n-cm$^2$

Film Thickness = 0.11 mm

$Fe^{+3}$ transfer, $P_{Fe}^+$ = 7-8 mg Fe/mF

CDLL-A5 durability in $FeCl_3$ at 80°C was excellent showing little or no change in any chemical or physical property of the film. However, the CDLL-A5 resin deteriorated structurally and lost IEC in the more aggressive redox environment, $2M CrCl_3$ at 80°C. At ambient temperature, $CrCl_3$ had little or no chemical or physical effect on the membrane (CDLL-A5H on Dynel fabric) and on CDLL-A5 on modacrylic fabric. (Table 12)

**Evaluation Summary - CDLL-A5 and A5H Membrane**

- Optimized for selectivity.

- Film thickness reduced to 0.11 mm with about 50% improvement in area resistivity.

- Excellent durability in $FeCl_3$ at 80°C and $CrCl_3$ at ambient temp.

- Large scale manufacture feasible using woven Dynel.

- Potential for thin film manufacture.
2.5 THE CP4L SYSTEM

The CP4L membrane is a copolymer of 4 vinylpyridine (4VP) and vinylbenzyl chloride (VBC). The resin structure consists of a vinyl backbone crosslinked by quaternary ammonium segments formed by the condensation reaction of the benzyl chloride part of VBC and the pyridine amino group (Figure 1a). The membrane sheet is formed in a one step synthesis similar to the procedure described in section 2.4.

The CP4L-A2 and A3 membranes have ranked highest of the candidate group in the overall significant physical and chemical properties. (Tables 1 and 8). The system produced the highest IEC, 4.5-5.0 meq/dgr, the lowest areas resistivity, $R_e^C$, 1.8 $\Omega$·cm$^{-2}$ and a low $Fe^{+3}$ transfer. In addition, the CP4L-A2 showed excellent structural and exchange group stability in both $FeCl_3$ and $CrCl_3$ at 80°C. Lab scale membranes have been produced on woven Dynel and on woven modacrylic.

The optimized CP4L-A2 membrane on modacrylic fabric had the following properties:

IEC = 5.30 meq/dgr (about 55% in strong base capacity)

Water Content = 31.8%

Area Resistivity, $R_e^C$ in 0.1N HCl = 1.8 $\Omega$·cm$^{-2}$

$Fe^{+3}$ transfer, $P_{Fe} = 4.8\times10^{-3}$ mg Fe/mF

The superior resistivity and good selectivity of the CP4L-A2 membrane relates to the unusually high ion exchange capacity achieved by the 4VP monomer. The fixed ion charge density or interstitial molality, $I_M$, of the resin was 11.4 meq/g H$_2$O. The highest $I_M$ obtained in the previous contract period was 7.5 meq/g H$_2$O (Table 10, NASA CR-134931). The interstitial molality is defined as the meq of exchange capacity per gram of resin water content.

The effectiveness of cation exclusion was demonstrated by the small change observed in CP4L-A2 area resistivity over the range of 0.1 to 6.0N HCl in the external solution and indicated that the CP4L membrane experienced
less H⁺ intrusion than the other candidate resins. (Table 14)

Lab scale manufacture of the CP4L was direct and easy. Large scale manufacture of the CP4L appears to be possible.

Although the modacrylic fabric produced excellent membrane films it was chemically sensitive to the CP4L monomers resulting in some fabric shrinkage and thickening of the end product film to 0.25 mm.

Evaluation Summary CP4L-A2 Membrane

- Optimized selectivity.
- Improved resistivity by reducing film gage to 0.25 mm.
- Has highest IEC and lowest area resistivity of candidate group.
- Excellent durability in both FeCl₃ and CrCl₃ at 80°C.
- Viable manufacture on lab scale and potential for large scale production.
2.6 A3L-97 MEMBRANE

The A3L-96 polymer is composed of 2 vinyl pyridine crosslinked by ethyleneglycol dimethacrylate. (Figure 1f). It was selected as the sixth candidate because of its anticipated ease of manufacture in a one step polymerization process and potentially low Fe$^{3+}$ transfer rate. The initial trial using Teflon fabric as backing was not successful. However, we expect to furnish samples of an optimized version on both Dynel and a thin synthetic fabric.

Evaluation Summary A3L-96 Membrane

- Durable membrane in redox environment at ambient temperature.
- Potential ease of manufacture in one step polymerization.
3.0 ALTERNATIVE MEMBRANE SYSTEMS

Under Task I (NAS 3-20108) we proposed to screen at least eight alternative membrane/polymer systems and select from this number those which showed good potential for improvement in selectivity and electrical resistivity in addition to ease of manufacture and durability in the redox environment. The method of film manufacture in most of the above systems was bulk polymerization of the monomers on synthetic fabric using heat and free radical initiators. In one system the membrane was formed by the amination of a commercial PVC film. (Table 9)

Two alternative membrane systems were advanced to candidate status.

(1) The CDL system - a copolymer of vinylbenzylchloride (VBC) and dimethaminoethylmethacrylate (DMAEMA)
(2) The CP4L system - a copolymer of VBC and 4-vinylpyridine (4VP)

The remaining proposed alternative membrane systems were explored and evaluated. Four systems have shown film manufacture viability and promising physical and chemical properties. These were:

(1) The CT system - a copolymer of VBC and tetraethylene pentamine (TEPA)
(2) The CTM system - a copolymer of VBC and N, N, N', N' tetramethyl ethylene diamine (TMEDA)
(3) The VC1-TP system - PVC film aminated with TEPA.

Three systems were rejected because of inability to manufacture films using the current bulk polymerization technology. These are:

(1) The CE system - a copolymer of VBC and ethylenediamine (EDA)
(2) The CD system - a copolymer of VBC and diethylene triamine (DETA)
(3) The CX system - a copolymer of 4VP and α,α' xylenedichloride (XDC)
(4) The SEM system - a copolymer of ethylene glycol dimethacrylate (EDGM) and sulfoethyl methacrylate (SEM)
3.1 THE CT SYSTEM

In this case, vinylbenzyl chloride (VBC) is used with polyalkylpolyamine (TEPA) providing both the needed crosslink segment. (Figure 2a) The CT resin is prepared by a two step process in which the active ingredients VBC and TEPA are reacted to form an aminovinyl intermediate. The intermediate is then polymerized by heat and initiator on synthetic fabric.

The initial membrane samples showed unusually high levels of weak base IEC in the range of 6-7 meq/dgr. However, the high $H_2O$ content of the membrane and severe resin erosion in acid indicated a weakly cross-linked polymer structure.

The application of higher cure temperatures and an increase in VBC did not sufficiently improve the resin stability for membranes prepared by saturation of woven fabrics. However, thin films of the CT resin bonded to non-woven substrates showed improved durability in acid solution, an effect which may be due to the greater continuous physical support provided by the mat fibers. The best non-woven backing in this regard was a polypropylene mat.

Evaluation Summary - CT System

- Highest IEC attained in program.
- Components have high reactivity.
- Shows potential for thin film manufacture on porous substrate.
3.2 THE CTM SYSTEM

A crosslinked structure is produced by the condensation of the benzyl-chloride group of VBC with both ends of the tertiary diamine, N, N, N', N' tetramethylethylene diamine (TMEDA). This forms quaternary exchange sites at the cross link segment. (Figure 2b)

The CTM membrane was prepared in a one step process. The monomers were mixed together in a solvent containing initiator. Hard, well cured films were produced when the monomer solution was rapidly polymerized. Gradual heating tended to produce undercured films. However, even the well cured membranes tended to erode and leak after several days standing in acid environment.

The CTM polymer system gave IEC values in the 4-5 meq/dgr range which consisted of over 90% in strong base capacity.

Evaluation Summary - CTM System

- One step polymerization with very reactive monomers.
- High IEC which is predominantly (90%) strong base capacity.
- Potential for thin film manufacture.
3.4 **THE SEM SYSTEM**

The SEM membrane/polymer system represents the sole cation selective membrane proposed in the current program. The SEM resin is a copolymer of sulfoethyl methacrylate (SEM) and the crosslinker ethylene glycol dimethacrylate (EGDM). (Figure 2g)

The trial samples as prepared on woven Dynel had good integrity and area resistivity in 0.1N HCl, $R^2 = 13.0 \text{ ohm-cm}^2$. The IEC and $H_2O$ content was 2.3 meq/dgr and 38% respectively.

The SEM system, however, was rejected from further consideration because of leakage failure during testing for Fe transfer in 2M FeCl$_3$ solution. All samples behaved similarly although the original films were apparently free of holes or cracks by inspection and testing with dye.

**Evaluation Summary - SEM**

- SEM membrane system not suitable because of resin failure in redox solution.
3.3 THE VC-TP SYSTEM

The VC-TP membrane system was the sole system proposed in the current program which was not produced by bulk polymerization of liquid monomers. The VC-TP membranes were prepared by the amination of thin commercial polyvinylchloride (PVC) film using tetraethylene pentamine (TEPA). The structure consists of PVC chains and pendant polyalkyl polyamine groups some of which may crosslink the PVC chains. The anion exchange groups are secondary and primary amines. (Figure 2c)

Tables 10 and 11 summarize the physical and chemical properties of the experimental VC-TP membranes produced in the program. A variety of commercial PVC films were tested comprising film thickness of 0.025 mm (1 mil) to 0.20 mm (8 mil) and with a plasticizer range of 7 to 30%.

As produced, the membranes tended to show low selectivity (excessive $\text{Fe}^{+3}$ transfer). With post treatment of the membranes in $\text{FeCl}_3$ solution and in air, the selectivity was improved but with resultant loss in IEC and conductivity. None of the usable film samples produced in the current program were recommended for testing at the NASA Lewis Center because of the relatively high $\text{Fe}^{+3}$ transfer rate.

Advantages of the VC-TP membrane were its film gage (0.025-0.20 mm) resulting in very low resistivities and good film strength and integrity. It tended to embrittle somewhat with prolonged heating.

Evaluation Summary - VC-TP Membranes

- Membrane as currently produced not suitable for redox application.
- Potential as conductive thin substrate for application of candidate polymer film.
3.5 THE CE, CD, AND CX SYSTEMS

The following polymer systems were found unworkable for direct and easy manufacture of useful homogeneous anion membrane films. These were the:

(1) CE System - copolymer of vinylbenzylchloride (VBC) and ethylenediamine (Figure 2d).

(2) CD System - copolymer of VBC and diethylene triamine (DETA) (Figure 2e).

(3) CX System - copolymer of 4 vinylpyridine (4VP) and CX, CX' dichloro-p-xylene. (Figure 2c)

Successful film manufacture using the bulk polymerization method required that the monomer-solvent constituents of the system be miscible and capable of stable homogeneous monomer solutions for fabric impregnation prior to polymerization and curing.

The components of the CE, CD and CX systems were generally incompatible in a wide variety of polar and non-polar solvents, separating into 2 or 3 phase solutions or producing insoluble precipitates during the mixing stage.
4.0 DURABILITY OF CANDIDATE MEMBRANES

The anion selective membranes studies in this program were composites of a variety of experimental ion-exchange resins and synthetic fabrics. Long term useful functioning of these membranes as cell separators in a redox system requires that the resin structure, ion exchange groups, and the supportive fabric have adequate long term stability and chemical resistance to the redox cell solutions.

The durability of the candidate membranes was tested by the immersion of membrane samples (3" in diameter) in 2M FeCl₃/1N HCl and in 2M CrCl₃/1N HCl solutions maintained at 80°C for a period of 1000 hours. At intervals of 100, 250, 500, and 1000 hours membrane samples were removed for inspection and analysis of chemical and physical properties.

Each membrane sample was characterized as follows:

(a) Visual inspection for obvious gross changes such as resin erosion, surface cracks, color, and flexibility.
(b) Non staining dye test for leak defects
(c) Burst strength or Mullen Burst Tester—this data is essentially a measure of the fabric durability as polyelectrolyte membranes have little or no self supportive strength
(d) Ion exchange capacity (IEC)
(e) Water content
(f) Resistivity in 0.1N HCl
(g) Fe⁺³ transfer rate

A summary of the durability test results is given in Table 12.

The CP4L-A2 membrane on woven modacrylic fabric ranked highest in all around durability. The CP4L-A2 showed little or no significant change in the essential functional and structural membrane properties in both FeCl₃ and CrCl₃ test solutions at 80°C. Sole alteration was the resin color which changed from a transparent colorless appearance to a dark opaque color but with no apparent detriment to any measurable chemical or physical property.

The A3L-B7 membrane on woven Dynel had similar good durability
in all functional properties in both redox environments but showed some film stiffness or brittleness by 100 hours which produced a small loss on film burst strength (15%).

The 103QZL and CDIL systems exhibited good durability in FeCl₃ but showed a substantial loss of selectivity and an increase in water content in C. l₃ at 80°C. Both effects indicated some structural deterioration or opening up of the polymer net-work. The CDIL resin which is cross-linked by a quaternary ammonium chloride showed a marked decrease in strong base IEC and a corresponding rise in weak base IEC, an effect caused by splitting of the carbon-nitrogen exchange groups. The major deterioration effects in the 103QZL and CDIL membranes occurred in the first 100 hour period of solution contact and little significant change in functional properties was measured thereafter from the 200 hour to the 1000 hour mark. The CDIL membranes experienced no embrittlement of stiffening and consequently showed no loss in burst strength (fabric strength) in either solution. At ambient temperature the CDIL showed excellent durability in the CrCl₃ test solution.

The durability data collected on the B2LDT-B2 was mix i. The B2LDT-B2 resin exhibited excellent structural and ion exchange group stability in FeCl₃ and CrCl₃ at the elevated temperature. The observed membrane deterioration was due to fabric failure. The low burst strength of the membrane containing woven Dynel was the result of damage to the backing during the amination step. The B2LDT-B2 membrane on woven Teflon, showed progressive increase in Fe³⁺ transfer leading eventually to severe leakage. The membrane failure in this case was most likely related to inadequate resin bonding to the Teflon yarn. The most successful and durable candidate polymer fabric composite films have been on Dynel and modacrylic backing materials.
5.0 MEMBRANE BACKING MATERIALS

Membrane electrical resistance is directly related to the thickness of the functional resin film. Major improvement or decrease in membrane resistance can be achieved for a particular optimized candidate polymer only by a substantial reduction in the resin film thickness.

Homogenous ion exchange resins are by themselves too fragile to yield a useful unbroken continuous sheet of reasonable size without the aid of a supportive substrate usually a fabric. The candidate membranes optimized for selectivity were manufactured on woven Dynel, a fabric with excellent resin compatibility and chemical durability but yielding finished membrane sheets 0.55 - 0.65 mm (25 mil) in thickness and area resistivities, \( R^c \), in the \( 1 \times 10^{	ext{ohm-cm}^2} \) range.

For the purpose of reducing membrane thickness, about 25 thin gage woven and non-woven fabrics were screened as backing material for membranes. These included modacrylic, Teflon, polypropylene and glass.

In the bulk polymerization method of membrane manufacture the backing fabric is saturated by the liquid monomer charge whose subsequent polymerization creates a resin-fabric composite sheet. The sheet thickness is determined by the fabric gage. In practice the finished membrane is usually somewhat thicker than the backing fabric due to swelling and penetration of the fibers by the monomers and solvent. A suitable fabric for membrane support must be chemically compatible, bond well with the resin and have physical and chemical stability in the manufacturing process. In addition, the support fabric must be thermally and chemically stable in the redox environment up to 80°C.

The woven and non woven fabrics considered in the test program yielded membrane films in the thickness range of 0.10 to .50 mm. The
corresponding resistivity (absolute) showed at best only a 2 to 3 fold improvement over the standard Dynel candidate membrane primarily due to the varying density of yarn or fiber construction of the backing materials. A major limitation in thin supported ion exchange films is that small defects which can be ignored in thicker films become exaggerated in thin films and can produce random pin-hole leaks. Consequently, thin resin films tend to require more densely constructed supports for strength and film continuity, which in turn tends to increase the overall membrane specific resistivity.

The compatibilities and stabilities of the backings tested were variable. Woven modacrylic gave good results in the CD1L and CP4L candidate systems. It experienced yarn shrinkage when immersed in the CP4L monomers producing a thicker gage film than anticipated, however, lab scale samples of the CP4L-A2 on modacrylic had excellent physical and chemical properties. The modacrylic fabric was not suitable for the more non-polar candidate polymer systems 103QZL, A3L and B2LDL because of partial solubility in the monomers.

Teflon yielded films with good physical appearance for the 103QZL, B2LDL and A3L systems but the problem of adequate resin-fabric bonding was not solved. The membrane yields were improved (lower incidence of random pinholes) by longer residence time of the fabric in the liquid monomers.

The Teflon fabric, however, ranked considerably below the Dynel and modacrylic in terms of uniformity and reliability of the membrane films. The A3L system membrane on Teflon in particular, developed severe leakage on standing in acid environment for several weeks, although as manufactured it exhibited reasonable film integrity. The 103QZL-B10 on Teflon showed fragility and tendency to develop leakage on testing.
Non-woven polypropylene mats showed some promise in the A3L systems, but behaved very poorly in the 103Q2L system.

Two special substrate materials, PVC foam sheet and melt blow polypropylene wettable mat indicated good bonding for the A3L system and for the more polar resin systems such as the CDIL.

Glass weaves produced film with excellent physical appearance on manufacture, however, glass fibers (E-grade) had very poor durability in acid. Astroglass, a high temperature resistance grade, and also glass with protective coatings or finish may be more satisfactory.
6.0 MEMBRANE RESISTIVITY IN NaCl AND HCl SOLUTIONS

The resistivity of the candidate membranes was measured as a function of concentration in HCl and NaCl solutions at 25°C using the liquid junction method. (NASA CR-134931 APPENDIX III) The measurements were taken over a range of 0.1 to 6.0 N in HCl and 0.1 to 5.0 N in NaCl. The NaCl solution was acidified to 0.01N in HCl in order to maintain the electrical conductivity of the weak base amino groups. The electrolytes were circulated and thermostated at 25 ± 0.2°C. The results are summarized in Tables 13 and 14 and Figures 3, 4, 5, & 6.

Ion selective membranes are electrically conductive by virtue of the fixed ionized sites in the resin matrix which permits movement, as in electrolyte solutions, of the mobile counterion.

Ion exchange resins also adsorb varying amounts of electrolyte (Donnan diffusion) depending on the physical and chemical properties of the resin, and the nature and composition of the external electrolyte. The membrane resistivity as measured in solution represents additive mobilities of the resin counter ions (Cl⁻) and any adsorbed electrolytes (HCl or NaCl).

Electrolyte exclusion is generally favored by a high ion exchange capacity, a high internal fixed charge density, and low resin porosity. Electrolyte exclusion is also favored in dilute concentrations, low valence of the counterions, and high valence of the co-ions in the external solution. The most selective membranes are those which are effective in excluding electrolyte at high concentration.

As expected, the membrane resistivity declined as the concentration of HCl increased producing greater electrolyte diffusion into the resin. The membrane with the highest porosity, the 103Q2L-B2 showed the greatest
drop in resistivity. Less resistance change occurred for those membranes having better selectivity and thus greater effectiveness in excluding cations. These were the CD1L-A5H10, A5-3 and the CP4L-A2-2 membranes. One measure of the membranes effectiveness in excluding the cation, $H^+$, was indicated by the ratio of $R$ at 0.1N HCl to $R$ at 6.0N HCl.

The smallest change in the ratio $R$ (0.1/$R$ (6.0) was shown by the candidates CD1L-A5 and CP4L-A2. These membranes have the highest IEC or ion charge density of the candidate group and should have high selectivity to anion transfer in strong acid solutions.

The membrane resistivities in NaCl solution (acidified) showed a smaller decline than in HCl but were ranked in the same order of ion exclusion effectiveness. The candidate membranes were better able to prevent the intrusion of Na$^+$ because of its lower mobility. The CP4L membrane showed a higher resistance at 5.0N NaCl than at 0.1 N NaCl. This unexpected increase may be due to an osmotic loss of $H_2O$ from the resin at the high external salt concentration.

At dilute electrolyte concentration (0.10 N) the membrane resistivities were approximately the same in either NaCl or HCl for each particular candidate. This resistance value represents closely the basic resistivity of the resin in the Cl$^-$ form as there is minimal contribution to the resin conductance by the adsorbed electrolyte. The more selective membranes, CD1L and CP4L, show a relatively flat conductivity response to increased electrolyte concentration indicating that very little electrolyte is being adsorbed by the resin.

Tables 15 and 16 compare specific resistance of the candidate membranes and the electrolyte solutions. The CD1L A5H-10 and CP4L-A2 membrane show a specific resistance very close to that of 0.10 N NaCl. The data indicates that as membrane selectivity approaches 100% effectiveness, the specific
resistance of the membrane (at equal IEC values) will tend to increase because of the more efficient exclusion of electrolyte particularly the acidic species. Further improvement in membrane selectivity will tend to increase the specific resistivity. Thus major reduction in absolute membrane resistance without selectivity loss will require a proportional reduction in membrane film thickness to counter balance the increase in resistivity.

The area resistivities of the thin film versions in each candidate system was reduced by a factor of 2 to 3.
7.0 $\text{Fe}^{+3}$ TRANSFER AS A FUNCTION OF $\text{FeCl}_3$ CONCENTRATION

The $\text{Fe}^{+3}$ transfer rate, $P_{\text{Fe}}$, was measured for several candidate membranes, the 103QZL-B2 and the CP4L-A2 at four different $\text{FeCl}_3$ concentrations: 0.5, 1.0, 2.0, and 4.0 N acidified 1N in HCl. Two other candidates, the 103QZL-B10 and the CD1L-AS-H-10 were tested at 0.5 and 2.0 and 4.0 N.

The amount of $\text{Fe}^{+3}$ transfer per unit of electric current was a measure of the membranes functional selectivity or efficiency under dynamic redox cell conditions. The test simulated a redox $\text{FeCl}_3$ half cell at a current density $CD = 60 \text{ mA/cm}^2$, in the charging mode (polarity) of cell operation. A detailed description of the test procedure and apparatus is presented in NASA CR 134931 (page 38, and Appendix IV).

The $\text{Fe}^{+3}$ transfer rate, remained approximately constant for all membranes in the electrolyte range of 0.5 to 2.0N, but increased substantially at the 4.0 N level. The 103QZL-B2, the membrane with the highest porosity, showed an $\text{Fe}^{+3}$ transfer rate of $127-233 \times 10^{-3} \text{ mg Fe/mF}$ at 4.0N $\text{FeCl}_3$ an eight fold increase from a base line of $18-30 \times 10^{-3} \text{ mg Fe/mF}$.

The most efficient membranes in the candidate series, the CP4L-A2, and CD1L-A5 showed only a three fold increase at 4.0N $\text{FeCl}_3$.

A summary of the data is given in Table 17.
8.0 $\text{Fe}^{+3}$ TRANSFER AS A FUNCTION OF CURRENT DENISTY

The variability of $\text{Fe}^{+3}$ transfer was measured as a function of current density for three membranes.

(1) the 103QZL-219S, a standard production membrane (Ionics, Inc.) with a high porosity relative to the optimized candidate systems

(2) A3L-A5 - low porosity candidate

(3) A3L-A6 - low porosity candidate

The variation in current density was 15 to 480 ma/cm$^2$ for the 103QZL-219S and 60 to 240 ma/cm$^2$ for the A3L-A5 and A6. The results were summarized in Table 18. We found that the $\text{Fe}^{+3}$ transfer (or loss) was greatly diminished above a CD=120 ma/cm$^2$ for the more porous membrane, 103QZL-B219S. At CD=480 the $P_{\text{Fe}}^+$ was $7.13 \times 10^{-3}$ mg Fe/mF a 500 fold reduction from the high Fe loss of about 1-4 mg Fe/mF at the lower current density values. (Figure 7)

The more selective and less porous membranes A3L-A5, A6 showed little or no change in $\text{Fe}^{+3}$ transfer with increase in the current density.

The extreme reduction in $\text{Fe}^{+3}$ transfer observed in the 103QZL-219S at high CD values could result from a polarization effect at the membrane solution interface. The high electric current demand could produce depletion of $\text{Fe}^{+3}$ in the interfacial solution film and make it less available for transfer. Replenishment of the depleted film by diffusion of electrolytes from the solution bulk would favor the more mobile $H^+$ ion which is present in high concentration.
The membrane types 103QZL-B-2P and A3L-37P, developed for NASA Lewis under contract number NAS3-20108, were prepared in sizes 20" x 42" and in quantities of six membranes each.

We statistically obtained samples from these small production runs by selecting, at random, three membranes from each, cutting analytical samples from each of the three (Labeled membranes A, B, and C for each membrane type) as follows:

For each membrane type (i.e., 103QZL-B2P or A3L-37P) there were developed a total of 15 typical samples, a small number (n) to be sure but still an effective sample variation to plot 3 sigma (3 ) production capability.

The four most important parameters (or properties) to be considered when planning membrane production capability are:

1. Ion Exchange Capacity, a measure in milliequivalent of dry resin of the exchangable resin counter (exchangable) ion.
2. Thickness in millimeters.
3. Water content on a wet membrane basis.
4. Resistivity - measured in ohm-cm$^2$ through the plane of the membrane.
In the case of the 103QZL-B2P and A3L-B7P membranes, only 5 samples each for a particular property have been made available due to very limited production. These have been listed in Tables 19, 20, and 21.

In the statistical analyses of the small lots of the two special membranes, we can see from Table 22 that our capability for manufacturing these new experimental membranes in a good tight specification range is good. While this evaluation is based upon a very small sampling, it is unlikely, based on past experience, that the range will increase much more than a factor of two when a large number of samples of similar material have been prepared.
10.0 CONCLUSIONS

- The CP4L-A2 membrane, a copolymer of 4 vinylpyridine and vinylbenzyl chloride, ranked highest in overall properties of selectivity, $^{+3}$ resistivity, and durability. The optimized properties were: Fe transfer rate = 4-8 mg Fe/mF, Resistivity, $R = 1.8$ ohm-cm$^2$ at 0.23 mm film thickness, and superior durability in FeCl$_3$ and CrCl$_3$ at 80°C.

- The optimized versions of the other candidate membranes were ranked in the following order: A3L-B7, 103QZL-B10, CD1L-A5, B2LDT-B2. Their optimized Fe$^{+3}$ transfer rates were in the range of 1-8 mg Fe/mF, and met the contract target Fe$^{+3}$ transfer rate of ~2 mg Fe/mF.

- The use of thin woven and non-woven synthetic fabrics as backing materials demonstrated a 2 to 3 fold improvement in membrane electrical resistance by reducing the functional film gage to about .10 to .30 mm range. Several experimental fabrics showed promise as backings or substrates, however, none attained the excellent durability and use reliability of the standard heavy gage woven Dynel (film gage=0.6 mm).

- The CP4L-A2, A3L-B7 and B2LDT-B2 candidate polymers showed excellent stability of resin structure and ion exchange groups in FeCl$_3$ and CrCl$_3$ at 80°C. (1000 hr. test)

- The CD1L-A5 and 103QZL-B10 membranes gave good durability in FeCl$_3$ at 80°C and in CrCl$_3$ at ambient temperature.

- At least three alternative membrane/polymer systems showed promise for future development because of low resistivity and/or high ion exchange capacities. These were the CT, CTM, and VC-TP systems.

- Large scale manufacturing capability (5.5 ft$^2$ per membrane) was successfully demonstrated for two candidate membrane systems, the A3L-B7 and the 103QZL-B2 on Dynel woven backing 183.

- Fe$^{+3}$ transfer rates of candidate membranes were not sensitive to variations in FeCl$_3$ concentration in the 0.5 to 2.0 M range but increased substantially at 4.0M FeCl$_3$.

- Variations in current density in the 60 to 480 ma/cm$^2$ range did not effect the Fe$^{+3}$ transfer rates in low porosity and high selectivity membranes. A large decrease in the transfer rate was observed in the more porous membrane 103QZL-219S above 120 ma/cm$^2$. 
11.0 RECOMMENDATIONS FOR FURTHER WORK

1. Attempt major reduction in absolute membrane resistivity by creation of thin candidate resin film on suitable backing or substrate.

2. Investigate methods of application of thin film onto various available synthetic substrate materials.
   The substrates would include -
   a. non-woven mats in polypropylene, polyethylene, Teflon, and carbon;
   b. porous or macro-reticular ion exchange membranes and films.

3. Investigate alternative polymer systems,
   a. heterogeneous solvent cast films (ion exchange resin and binder)
   b. systems with IEC
      CT-copolymer VBC and TEPA
      CTM-copolymer VCB and TMEDA
      with emphasis upon the reaction of VBC with non sterically hindered polyamines.

4. Evaluate above thin film and alternative systems for resistivity, resistivity, and durability.

5. Reduce cation transfer in optimized candidate membranes to virtual zero level by creation of high density surface film.
ABSTRACT

Experimental anion permselective membranes were improved and characterized for use as separators in a chemical redox power storage cell being developed at the NASA Lewis Research Center. The goal of minimal Fe$^{+3}$ ion transfer was achieved for each candidate membrane system. Minimal membrane resistivity was demonstrated by reduction of film thickness using synthetic backing materials but usefulness of thin membranes was limited by the scarcity of compatible fabrics. The most durable and useful backing fabrics were modacrylics. One membrane, a copolymer of 4 vinylpyridine and vinylbenzylchloride was outstanding in overall electrochemical and physical properties. Long term (1000 hr) membrane chemical and thermal durability in redox environment was shown by three candidate polymers and two membranes. The remainder had good durability at ambient temperature. Manufacturing capability was demonstrated for large scale production of membrane sheets 5.5 ft$^2$ in area for two candidate systems.
### SYMBOLS

<table>
<thead>
<tr>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho^J$ Resistivity by liquid junction method</td>
<td>ohm-cm</td>
</tr>
<tr>
<td>$R^J$ Area resistance by liquid junction method</td>
<td>ohm-cm$^2$</td>
</tr>
<tr>
<td>$\rho^C$ Resistivity by contact probe method</td>
<td>ohm-cm</td>
</tr>
<tr>
<td>$R^C$ Area resistance by contact probe method</td>
<td>ohm-cm$^2$</td>
</tr>
<tr>
<td>$P_{Fe}^+$ Permeation factor for Fe in the charging mode</td>
<td>mg Fe/mF</td>
</tr>
<tr>
<td>$mF$ millifaraday</td>
<td>$96.5 \times 10^3$ ma-sec</td>
</tr>
<tr>
<td>IEC Ion exchange capacity</td>
<td>meq/dry gram resin</td>
</tr>
<tr>
<td>$I^M$ Interstitial molality</td>
<td>meq/gm $H_2O$</td>
</tr>
<tr>
<td>Membrane</td>
<td>Fabric Backing</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>103Q2L-2</td>
<td>Dynel</td>
</tr>
<tr>
<td>103Q2L-2</td>
<td>Teflon</td>
</tr>
<tr>
<td>103Q2L-810</td>
<td>Dynel</td>
</tr>
<tr>
<td>103Q2L-810</td>
<td>Teflon</td>
</tr>
<tr>
<td>A3L-77</td>
<td>Dynel</td>
</tr>
<tr>
<td>A3L-77</td>
<td>Teflon</td>
</tr>
<tr>
<td>821DT-52</td>
<td>Dynel</td>
</tr>
<tr>
<td>821DT-52</td>
<td>Teflon</td>
</tr>
<tr>
<td>CD1L-5H</td>
<td>Dynel</td>
</tr>
<tr>
<td>CD1L-5</td>
<td>Nitrile</td>
</tr>
<tr>
<td>CP1L-A1</td>
<td>Dynel</td>
</tr>
<tr>
<td>CP1L-A2</td>
<td>Nitrile</td>
</tr>
</tbody>
</table>

1. Durability Key
1- Good, no change in membrane properties
2- Fair to good, increase in Fe transfer but stable after 100 hours
3- Fair, continuing change in IEC, water content, or Fe transfer
4- Poor, multiple leaks

2. 821DT-52 Resin Properties (IEC, H<sub>2</sub>O stable in both FeCl<sub>3</sub> and CrCl<sub>3</sub>)
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Monomer Formulation</th>
<th>Polymer Batch</th>
<th>IEC (meq/dry g)</th>
<th>H2O (%)</th>
<th>$\mathbf{R}_p^2$ in 0.1N HCl (ohm-cm²)</th>
<th>$\mathbf{R}_q^2$ in 0.01 M NaCl (ohm-cm²)</th>
<th>Fe Transfer $\mu_{Fe}$ (mg Fe/m²x10⁻³)</th>
<th>Resin Condition</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>103QGL-B2</td>
<td>.35 .35</td>
<td>1</td>
<td>2.13</td>
<td>30.1</td>
<td>10.5</td>
<td>----</td>
<td>22-39</td>
<td>none</td>
<td>none Flexible Candidate</td>
</tr>
<tr>
<td>103QGL-B10</td>
<td>.35 .30</td>
<td>1</td>
<td>2.24</td>
<td>25.4</td>
<td>10.6</td>
<td>----</td>
<td>2-1</td>
<td>none</td>
<td>none Flexible Candidate</td>
</tr>
<tr>
<td>103QGL-A1</td>
<td>.35 .40</td>
<td>1</td>
<td>2.09</td>
<td>36.5</td>
<td>7.4</td>
<td>----</td>
<td>210</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A2</td>
<td>.35 .35</td>
<td>1</td>
<td>2.00</td>
<td>26.5</td>
<td>7.4</td>
<td>----</td>
<td>130</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A1</td>
<td>.35 .40</td>
<td>1</td>
<td>2.82</td>
<td>26.5</td>
<td>7.4</td>
<td>----</td>
<td>140</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A3</td>
<td>.30 .30</td>
<td>1</td>
<td>2.74</td>
<td>27.7</td>
<td>7.6</td>
<td>----</td>
<td>120</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A4</td>
<td>.30 .35</td>
<td>1</td>
<td>3.05</td>
<td>38.5</td>
<td>6.3</td>
<td>----</td>
<td>110</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A5</td>
<td>.25 .30</td>
<td>1</td>
<td>3.20</td>
<td>32.6</td>
<td>4.6</td>
<td>----</td>
<td>120</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A6</td>
<td>.20 .30</td>
<td>1</td>
<td>3.97</td>
<td>32.6</td>
<td>4.6</td>
<td>----</td>
<td>110</td>
<td>none</td>
<td>none Flexible</td>
</tr>
<tr>
<td>103QGL-A7</td>
<td>.35 .25</td>
<td>1</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>severe severe Stiff</td>
</tr>
<tr>
<td>103QGL-A8</td>
<td>.35 .20</td>
<td>1</td>
<td>1.01</td>
<td>10.5</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>severe severe Stiff</td>
<td>unaminated high elec. resist. NG</td>
</tr>
<tr>
<td>103QGL-A9</td>
<td>.35 .15</td>
<td>1</td>
<td>0.75</td>
<td>6.9</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>severe severe Stiff</td>
<td>unaminated high elec. resist. NG</td>
</tr>
</tbody>
</table>

**Key:**
- HP: volume fraction of non-polymerizable solvent
- XLI-DVB: molar fraction in monomers (crosslink factor)
- $\mathbf{R}_p^2$: contact resistivity in 0.1N HCl
- $\mathbf{R}_q^2$: contact resistivity in 0.01 M NaCl
- $\mu_{Fe}$: Fe transfer at CD = 60 mA/cm²
### TABLE 3.

**CANDIDATE ANION MEMBRANES PREPARED WITH DVB**

**Backing Material** - 4 oz woven dynel cloth

**Film Thickness** - 0.55-0.65 mm

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Cross-Linker</th>
<th>Linear Monomer</th>
<th>Post Reaction</th>
<th>TEC (mg/oz)</th>
<th>H₂O %</th>
<th>@25°C (ohm·cm²)</th>
<th>@80°C</th>
<th>Fe Transfer (mg Fe/m²x10⁻³)</th>
<th>Physical Condition of Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>103 QZL-A2-3</td>
<td>DVB</td>
<td>VBC</td>
<td>amination in TMA</td>
<td>2.98</td>
<td>32.0</td>
<td>4.72</td>
<td>1.73</td>
<td>12-40</td>
<td>A</td>
</tr>
<tr>
<td>103 QZL-B2</td>
<td>DVB</td>
<td>VBC</td>
<td>amination in TMA</td>
<td>2.25</td>
<td>30.6</td>
<td>4.17</td>
<td>2.76</td>
<td>28-46</td>
<td>A</td>
</tr>
<tr>
<td>103 QZL-B10</td>
<td>DVB</td>
<td>VBC</td>
<td>amination in TMA</td>
<td>2.31</td>
<td>25.8</td>
<td>6.40</td>
<td>3.96</td>
<td>10-20</td>
<td>A</td>
</tr>
<tr>
<td>A3L-A5-2</td>
<td>DVB</td>
<td>2-VP</td>
<td>none</td>
<td>3.38</td>
<td>27.5</td>
<td>10.4</td>
<td>4.92</td>
<td>11-25</td>
<td>B</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>DVB</td>
<td>2-VP</td>
<td>none</td>
<td>3.16</td>
<td>31.6</td>
<td>6.45</td>
<td>2.77</td>
<td>08-13</td>
<td>A</td>
</tr>
</tbody>
</table>

**Key:**

- DVB: Divinylbenzene
- VBC: Vinylbenzylchloride
- 2-VP: 2-vinylpyridine
- TMA: Trimethylamine

**R̅₆** Resistivity (ohm·cm²) by liquid junction in 1.0 M HCl at 25 and 80°C

**Physical Condition of film**

- **A** = good physical properties, leak free, well coated
- **B** = fair physical properties, some leaks, contains cracks.
### TABLE 4.

A3L MEMBRANE SYSTEM - PROPERTIES AS A FUNCTION OF SYNTHESIS VARIABLES

Copolymer - 2 vinylpyridine, divinylbenzene

Film Thickness - .60-.70 mm, film backing-4 oz Dynel cloth

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Monomer Formulation</th>
<th>IEC (meq/dgr)</th>
<th>H₂O (%)</th>
<th>R⁺ (_{\text{Fe}}) (ohm-cm²)</th>
<th>Fe Transfer</th>
<th>Erosion</th>
<th>Leaks</th>
<th>Other</th>
<th>Remarks</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3L-B7</td>
<td>.25</td>
<td>.30</td>
<td>3.40</td>
<td>.1N HCl 9.1</td>
<td>1-2</td>
<td>None</td>
<td>None</td>
<td>Whole</td>
<td>Candidate</td>
<td></td>
</tr>
<tr>
<td>A3L-A1</td>
<td>.35</td>
<td>.40</td>
<td>3.22</td>
<td>36.6</td>
<td>11.3</td>
<td>440</td>
<td>None</td>
<td>Few</td>
<td>Cracks</td>
<td></td>
</tr>
<tr>
<td>A3L-A3</td>
<td>.35</td>
<td>.50</td>
<td>3.70</td>
<td>36.9</td>
<td>10.1</td>
<td>610</td>
<td>None</td>
<td>None</td>
<td>Whole</td>
<td></td>
</tr>
<tr>
<td>A3L-A2</td>
<td>.30</td>
<td>.40</td>
<td>3.14</td>
<td>31.9</td>
<td>11.8</td>
<td>140</td>
<td>None</td>
<td>Few</td>
<td>Cracks</td>
<td></td>
</tr>
<tr>
<td>A3L-A4</td>
<td>.30</td>
<td>.35</td>
<td>4.63</td>
<td>31.9</td>
<td>7.3</td>
<td>42</td>
<td>None</td>
<td>Few</td>
<td>Cracks, Low Fe Transfer</td>
<td>Low Fe Transfer</td>
</tr>
<tr>
<td>A3L-A6</td>
<td>.30</td>
<td>.30</td>
<td>5.60</td>
<td>33.9</td>
<td>6.2</td>
<td>37</td>
<td>None</td>
<td>None</td>
<td>Whole, Low Fe Transfer, no cracks</td>
<td>Low Fe Transfer</td>
</tr>
<tr>
<td>A3L-A5</td>
<td>.25</td>
<td>.35</td>
<td>4.43</td>
<td>26.3</td>
<td>11.2</td>
<td>7</td>
<td>None</td>
<td>None</td>
<td>Cracks, Low Fe Transfer</td>
<td>Low Fe Transfer</td>
</tr>
<tr>
<td>A3L-A7</td>
<td>.25</td>
<td>.30</td>
<td>3.66</td>
<td>24.6</td>
<td>11.2</td>
<td>-</td>
<td>Slight Few</td>
<td>Cracks</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>A3L-A8</td>
<td>.20</td>
<td>.30</td>
<td>3.71</td>
<td>25.3</td>
<td>7.9</td>
<td>8</td>
<td>None</td>
<td>Few</td>
<td>Cracks, Low Fe Transfer</td>
<td>Low Fe Transfer</td>
</tr>
<tr>
<td>A3L-A9</td>
<td>15</td>
<td>.30</td>
<td>3.49</td>
<td>23.4</td>
<td>8.9</td>
<td>10</td>
<td>None</td>
<td>Few</td>
<td>Cracks, Low Fe Transfer</td>
<td>Low Fe Transfer</td>
</tr>
</tbody>
</table>

Key:  

\( f_{\text{NP}} \) = volume fraction of non-polymer solvent;  
\( f_{\text{XL}} \) = DVB molar fraction in monomers (crosslink factor);  
\( R_{\text{Fe}} \) = contact resistivity in 0.1 N HCl;  
\( P_{\text{Fe}}^+ \) = Fe transfer at COD-60 ma/cm²
### TABLE 5.

**A3L-B7 MEMBRANES ON VARIOUS WOVEN AND NON-WOVEN BACKING MATERIALS**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Fiber and Construction&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Membrane Thickness (mm)</th>
<th>Area Resistivity&lt;sup&gt;2&lt;/sup&gt; ( R_s ) in 0.1N HCl ((\text{n-cm}^2))</th>
<th>Area Resistivity ( R_s ) in 1.0N HCl @ 225°C ((\text{n-cm}^2))</th>
<th>Physical Properties as Manufactured</th>
<th>Film Uniformity&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dynel-W</td>
<td>0.60</td>
<td>9.5</td>
<td>6.5</td>
<td>None</td>
<td>Good</td>
<td>Best all around fabric</td>
</tr>
<tr>
<td>2</td>
<td>Teflon-W</td>
<td>0.25</td>
<td>5.5</td>
<td>---</td>
<td>Few&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Good</td>
<td>Potential backing, need improved adhesion</td>
</tr>
<tr>
<td>3</td>
<td>Glass-W</td>
<td>0.09</td>
<td>2.8</td>
<td>---</td>
<td>Few</td>
<td>Good</td>
<td>Weakens in acid</td>
</tr>
<tr>
<td>4</td>
<td>Glass-W</td>
<td>0.11</td>
<td>4.6</td>
<td>---</td>
<td>Few</td>
<td>Good</td>
<td>Weakens in acid</td>
</tr>
<tr>
<td>5</td>
<td>Glass-W</td>
<td>0.15</td>
<td>6.2</td>
<td>---</td>
<td>Few</td>
<td>Good</td>
<td>Weakens in acid</td>
</tr>
<tr>
<td>6</td>
<td>Glass-W</td>
<td>0.12</td>
<td>4.0</td>
<td>---</td>
<td>Many</td>
<td>Good</td>
<td>Weakens in acid</td>
</tr>
<tr>
<td>7</td>
<td>PP-NW</td>
<td>0.12</td>
<td>4.6</td>
<td>1.7</td>
<td>None&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Poor</td>
<td>Not suitable</td>
</tr>
<tr>
<td>8</td>
<td>PP.-NW</td>
<td>0.15</td>
<td>6.3</td>
<td>---</td>
<td>None</td>
<td>Fair</td>
<td>Potential substrate or backing</td>
</tr>
<tr>
<td>9</td>
<td>PP.-NW</td>
<td>0.37</td>
<td>9.1</td>
<td>4.4</td>
<td>None</td>
<td>Fair</td>
<td>Potential substrate or backing</td>
</tr>
<tr>
<td>10</td>
<td>PP.-NW</td>
<td>0.20</td>
<td>11.1</td>
<td>3.0</td>
<td>None</td>
<td>Fair</td>
<td>Not suitable</td>
</tr>
<tr>
<td>11</td>
<td>Modacrylic-W</td>
<td>---</td>
<td>----</td>
<td>---</td>
<td>Not-suitable-partially dissolves</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>PP-NW</td>
<td>0.49</td>
<td>4.1</td>
<td>3.9</td>
<td>Many</td>
<td>Fair</td>
<td>Not suitable</td>
</tr>
<tr>
<td>13</td>
<td>PP-NW</td>
<td>0.32</td>
<td>4.6</td>
<td>2.9</td>
<td>Many</td>
<td>Good</td>
<td>Not suitable</td>
</tr>
<tr>
<td>14</td>
<td>PP-NW</td>
<td>0.12</td>
<td>7.4</td>
<td>---</td>
<td>Many</td>
<td>Fair</td>
<td>Not suitable</td>
</tr>
<tr>
<td>15</td>
<td>PP-NW</td>
<td>0.05</td>
<td>4.3</td>
<td>---</td>
<td>Many</td>
<td>Fair</td>
<td>Not suitable</td>
</tr>
<tr>
<td>16</td>
<td>PP-NW</td>
<td>0.24</td>
<td>----</td>
<td>3.9</td>
<td>Many</td>
<td>Fair</td>
<td>Not suitable</td>
</tr>
<tr>
<td>17</td>
<td>PP-NW</td>
<td>----</td>
<td>----</td>
<td>---</td>
<td>Many</td>
<td>Fair</td>
<td>Not suitable</td>
</tr>
<tr>
<td>18</td>
<td>PP-NW</td>
<td>0.25</td>
<td>----</td>
<td>3.66</td>
<td>None</td>
<td>Fair</td>
<td>Potential backing or substrate</td>
</tr>
</tbody>
</table>

<sup>1</sup>W=Woven; N=Non Woven Mat; PP=Polypropylene

<sup>2</sup>Film Uniformity
- Good=Resin coating smooth, film lies flat
- Fair=Rough uneven resin coating

<sup>3</sup>Severe leakage on standing in acid (1-2 mo)
TABLE 6.

B2LDT MEMBRANE SYSTEM: PROPERTIES AS FUNCTION OF SYNTHESIS VARIABLES

Copolymer - Vinylbenzylchloride, divinyl benzene

Post amination in diethylenetriamine
Film thickness - .60-.70 mm, film backing -

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Monomer Formulation</th>
<th>Weak Base</th>
<th>H₂O (%)</th>
<th>Fe Transfer</th>
<th>Resin Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f XL f NP</td>
<td>IEC (meq/dgr)</td>
<td>0.1N HCl (ohm-cm)²</td>
<td>p⁺ Fe mg Fe/Mg x 10⁻³</td>
<td>Erosion</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>.35 .35</td>
<td>3.53</td>
<td>29.9</td>
<td>8.7</td>
<td>1-2</td>
</tr>
<tr>
<td>B2LDT-A1</td>
<td>.35 .40</td>
<td>5.31</td>
<td>24.2</td>
<td>9.1</td>
<td>8</td>
</tr>
<tr>
<td>B2LDT-A2</td>
<td>.35 .35</td>
<td>5.23</td>
<td>28.0</td>
<td>7.1</td>
<td>10</td>
</tr>
<tr>
<td>B2LDT-A3</td>
<td>.30 .30</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>B2LDT-A4</td>
<td>.30 .35</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>B2LDT-A5</td>
<td>.25 .30</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>18.3</td>
</tr>
<tr>
<td>B2LDT-A6</td>
<td>.20 .30</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>39.1</td>
</tr>
<tr>
<td>B2LDT-A7</td>
<td>.35 .25</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>B2LDT-A8</td>
<td>.35 .20</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>B2LDT-A9</td>
<td>.35 .15</td>
<td>----</td>
<td>----</td>
<td>33.0</td>
<td>7.72</td>
</tr>
</tbody>
</table>

Key:
- *f* NP = volume fraction of non-polymer solvent;
- *f* XL = DVB molar fraction in monomers (crosslink factor)
- *R*ₜ = contact resistivity in 0.1 N HCl
- *P⁺ Fe = Fe transfer at CD = 60 ma/cm²
TABLE 7.

CDIL MEMBRANE SYSTEM - SUMMARY
Copolymers - Vinylbenzylchloride, Dimethylaminoethylmethacrylate
Fabric Backing - Woven Dynel
Film Thickness - 0.60mm

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Synthesis Method</th>
<th>Monomer Formulation</th>
<th>Fe Transfer $P^+_Fe$ $mg Fe/mP \times 10^{-3}$</th>
<th>Resistivity $R_C$ in 0.1N HCl ($\Omega$-cm$^2$)</th>
<th>IEC (meg/dgr)</th>
<th>H$_2$O Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDIL-A1</td>
<td>1 Step</td>
<td>.30 1.5</td>
<td>17</td>
<td>9.3</td>
<td>4.44</td>
<td>42.4</td>
</tr>
<tr>
<td>CDIL-A2</td>
<td>1 Step</td>
<td>.30 2.0</td>
<td>41</td>
<td>5.2</td>
<td>4.26</td>
<td>39.4</td>
</tr>
<tr>
<td>CDIL-A3</td>
<td>1 Step</td>
<td>.30 2.5</td>
<td>21</td>
<td>5.2</td>
<td>4.04</td>
<td>37.3</td>
</tr>
<tr>
<td>CDIL-A4</td>
<td>1 Step</td>
<td>.30 3.0</td>
<td>49</td>
<td>5.2</td>
<td>5.06</td>
<td>40.1</td>
</tr>
<tr>
<td>CDIL-A5</td>
<td>1 Step</td>
<td>.25 2.0</td>
<td>8</td>
<td>5.2</td>
<td>4.18</td>
<td>32.9</td>
</tr>
<tr>
<td>CDIL-A6</td>
<td>1 Step</td>
<td>.20 2.0</td>
<td>14</td>
<td>6.2</td>
<td>4.16</td>
<td>35.1</td>
</tr>
<tr>
<td>CDIL-A7</td>
<td>1 Step</td>
<td>.50 2.0</td>
<td>--</td>
<td>---</td>
<td>4.39</td>
<td>49.0</td>
</tr>
<tr>
<td>CDIL-A5H</td>
<td>2 Step</td>
<td>.25 2.0</td>
<td>4</td>
<td>6.5</td>
<td>4.03</td>
<td>31.2</td>
</tr>
<tr>
<td>CDIL-A6H</td>
<td>2 Step</td>
<td>.20 2.0</td>
<td>5</td>
<td>7.3</td>
<td>4.29</td>
<td>32.1</td>
</tr>
<tr>
<td>CDIL-A8H</td>
<td>2 Step</td>
<td>.40 2.0</td>
<td>--</td>
<td>---</td>
<td>4.18</td>
<td>42.0</td>
</tr>
</tbody>
</table>

Key: $f_{NP} =$ Volume fraction of non-polymerizable solvent
$f_{MR} =$ Molar ratio DMAEMA/VBC
$P^+_Fe =$ Fe Transfer at CD = 60 ma/cm$^2$
TABLE 8.
VARIATIONS IN CP POLYMER SYSTEM - PHYSICAL & CHEMICAL PROPERTIES OF MEMBRANE

Monomers - vinylbenzyl chloride, 4-vinylpyridine
\( f_{NP} = 0.25 \)

Fabric Support - Dynel

Membrane size - 5" x 5"

<table>
<thead>
<tr>
<th>Membrane Sample</th>
<th>Vinyl Pyridine Monomer</th>
<th>Molar Ratio, ( M_R ) VP/VBC</th>
<th>IEC (meq/dgr)</th>
<th>% Total Strong Weak</th>
<th>( R^2 ) in 0.1 N HCl (ohm-cm(^2))</th>
<th>Fe Transfer, ( P_{Fe}^+ ) (mg Fe/mF( \times 10^{-3} ))</th>
<th>Physical Condition of Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP4L-A1</td>
<td>4 VP</td>
<td>4</td>
<td>6.32</td>
<td>2.06 4.27</td>
<td>42.9</td>
<td>2.4</td>
<td>severe few pinholes very flexible</td>
</tr>
<tr>
<td>CP4L-A2</td>
<td>4 VP</td>
<td>2</td>
<td>5.09</td>
<td>2.85 2.24</td>
<td>26.9</td>
<td>4.2</td>
<td>moderate few pinholes few cracks</td>
</tr>
<tr>
<td>CP4L-A3</td>
<td>4 VP</td>
<td>1.5</td>
<td>4.67</td>
<td>2.79 1.88</td>
<td>23.7</td>
<td>5.8</td>
<td>slight few pinholes few small cracks</td>
</tr>
<tr>
<td>CP4L-A4</td>
<td>4 VP</td>
<td>1.3</td>
<td>4.39</td>
<td>2.77 1.62</td>
<td>21.2</td>
<td>6.5</td>
<td>slight few pinholes few small cracks</td>
</tr>
<tr>
<td>CP4L-A5</td>
<td>4 VP</td>
<td>1.2</td>
<td>4.21</td>
<td>2.63 1.58</td>
<td>10.8</td>
<td>5.5</td>
<td>slight few pinholes Polymer fragi develops crac with slight pressure</td>
</tr>
<tr>
<td>CP4L-A6</td>
<td>4 VP</td>
<td>1.0</td>
<td>3.71</td>
<td>2.30 1.41</td>
<td>23.4</td>
<td>10.2</td>
<td>none few pinholes slightly stif</td>
</tr>
<tr>
<td>CP4L-A2(^1)</td>
<td>4 VP</td>
<td>2</td>
<td>4.63</td>
<td>2.25 2.38</td>
<td>37.4</td>
<td>---</td>
<td>none few pinholes mod. flexible</td>
</tr>
<tr>
<td>CP4L-A3(^1)</td>
<td>4 VP</td>
<td>1.5</td>
<td>4.61</td>
<td>3.14 1.47</td>
<td>31.2</td>
<td>4.6</td>
<td>none none flexible</td>
</tr>
</tbody>
</table>

\(^1\) On Modacrylic Woven Backing - Film Thickness = .25 mm.
<table>
<thead>
<tr>
<th>Membrane or Polymer System</th>
<th>Polymer Composition</th>
<th>Method of Film Manufacture</th>
<th>Status of Membrane</th>
<th>Synthesis Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDIL</td>
<td>VBC-DMAEMA</td>
<td>Bulk Polymerization of monomers on fabric</td>
<td>Candidate, High IEC, Good Selectivity, and resistivity</td>
<td>See Table 1.</td>
</tr>
<tr>
<td>CP4L</td>
<td>VBC-4VP</td>
<td>as above</td>
<td>Candidate as above</td>
<td>See Table 1.</td>
</tr>
<tr>
<td>CP2L</td>
<td>VBC-2VP</td>
<td>as above</td>
<td>Not recommended-2VP less reactive than 4VP</td>
<td>None</td>
</tr>
<tr>
<td>CE</td>
<td>VBC-EDA</td>
<td>No film, components incompatible, insoluble intermediate</td>
<td>Not recommended</td>
<td>None</td>
</tr>
<tr>
<td>CT</td>
<td>VBC-TEPA</td>
<td>Bulk Polymer on fabric</td>
<td>Potential candidate, Very high IEC 6-7 meq/dgr failure by resin erosion</td>
<td>Increase in cross linking and use in thinner films on non woven substrates</td>
</tr>
<tr>
<td>CTM</td>
<td>VBC-TMEDA</td>
<td>Bulk Polymer on fabric</td>
<td>Potential candidate, High IEC- 5 meq/dgr failure by resin erosion</td>
<td>as above</td>
</tr>
<tr>
<td>SEM</td>
<td>EGDM-SEM</td>
<td>Bulk Polymer on fabric</td>
<td>Not Recommended, medium IEC 2.5 meq/dgr High conductivity, leak failure in redox conditions</td>
<td></td>
</tr>
<tr>
<td>VCI-TP</td>
<td>PVC Film-animated with TEPA</td>
<td>Bulk Polymer on fabric</td>
<td>Potential candidate, High conductivity in thin film, but selectivity poor</td>
<td>Substrate for candidate resin</td>
</tr>
<tr>
<td>CX</td>
<td>4VP-XDC</td>
<td>No film, insoluble intermediate formed in monomer solution</td>
<td>Not recommended</td>
<td>None</td>
</tr>
</tbody>
</table>
### TABLE 10.

**POST-TREATMENT OF 3-PVC MEMBRANES**

PVC Films Aminated in TEPA,

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (mm)</th>
<th>Post-Treatment</th>
<th>Transfer $P_{Fe}^m$ (mg Fe/mF)</th>
<th>IEC (meq/dgr)</th>
<th>$H_2O$ (%)</th>
<th>$R_p^g$ in 0.1M HCl (ohm-cm$^2$)</th>
<th>Physical Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC2TP-B1</td>
<td>.05</td>
<td>Orig. Sample</td>
<td>2.25</td>
<td>3.02</td>
<td>27.6</td>
<td>0.20</td>
<td>Strong, Flexible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>0.13</td>
<td>1.52</td>
<td>12.7</td>
<td>1.34</td>
<td>Strong, Flexible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>Brittle, Split</td>
</tr>
<tr>
<td>VC3TP-B1</td>
<td>.05</td>
<td>Orig. Sample</td>
<td>1.92</td>
<td>2.76</td>
<td>26.6</td>
<td>0.18</td>
<td>Strong, Flexible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>0.28</td>
<td>1.46</td>
<td>20.0</td>
<td>1.03</td>
<td>Strong, Flexible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>0.014</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>Brittle</td>
</tr>
<tr>
<td>VC4TP-B1</td>
<td>.04</td>
<td>Orig. Sample</td>
<td>0.80</td>
<td>2.45</td>
<td>21.3</td>
<td>0.26</td>
<td>Strong, Flexible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>0.47</td>
<td>1.39</td>
<td>11.4</td>
<td>1.72</td>
<td>Strong, Flexible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>Leaks, Brittle</td>
</tr>
</tbody>
</table>

Post-Treatment applied to same sample:

A. in 2M FeCl$_3$/1M HCl, for 148 hrs at 80°C;

B. in air, for 1 hr at 110°C
TABLE 11.

MEMBRANE PROPERTIES: AMINATED POLYVINYLCLOLORIDE FILM

amination reagent - 100% tetraethylene pentamine

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Film Thickness (mm)</th>
<th>Plasticizer Content (%)</th>
<th>Reaction Conditions</th>
<th>Weak Base IEC (meq/dgr)</th>
<th>H₂O (%)</th>
<th>Rᶜ (ohm-cm²)</th>
<th>P⁺ Fe (mg Fe/mF)</th>
<th>Physical Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC1TP-A1</td>
<td>0.20</td>
<td>30</td>
<td>A</td>
<td>2.28</td>
<td>29.6</td>
<td>0.77</td>
<td>----</td>
<td>Flexible, Strong</td>
</tr>
<tr>
<td>VC1TP-B1</td>
<td>0.20</td>
<td>30</td>
<td>B</td>
<td>2.67</td>
<td>32.7</td>
<td>0.81</td>
<td>----</td>
<td>as above</td>
</tr>
<tr>
<td>VC2TP-A1</td>
<td>0.05</td>
<td>30</td>
<td>A</td>
<td>2.26</td>
<td>21.1</td>
<td>0.28</td>
<td>----</td>
<td>as above</td>
</tr>
<tr>
<td>VC2TP-B1</td>
<td>0.05</td>
<td>30</td>
<td>B</td>
<td>3.02</td>
<td>27.6</td>
<td>0.20</td>
<td>2.35</td>
<td>as above</td>
</tr>
<tr>
<td>VC3TP-A1</td>
<td>0.05</td>
<td>24</td>
<td>A</td>
<td>2.38</td>
<td>24.0</td>
<td>0.34</td>
<td>----</td>
<td>as above</td>
</tr>
<tr>
<td>VC3TP-B1</td>
<td>0.05</td>
<td>24</td>
<td>B</td>
<td>2.76</td>
<td>26.6</td>
<td>0.18</td>
<td>1.93</td>
<td>as above</td>
</tr>
<tr>
<td>VC4TP-A1</td>
<td>0.04</td>
<td>15</td>
<td>A</td>
<td>2.38</td>
<td>20.4</td>
<td>0.30</td>
<td>----</td>
<td>as above</td>
</tr>
<tr>
<td>VC4TP-B1</td>
<td>0.04</td>
<td>15</td>
<td>B</td>
<td>2.45</td>
<td>21.3</td>
<td>0.26</td>
<td>0.80</td>
<td>as above</td>
</tr>
<tr>
<td>VC5TP-A1</td>
<td>0.025</td>
<td>7-10</td>
<td>A</td>
<td>2.34</td>
<td>16.8</td>
<td>0.25</td>
<td>----</td>
<td>Brittle; tears easily</td>
</tr>
<tr>
<td>VC5TP-B1</td>
<td>0.25</td>
<td>7-10</td>
<td>B</td>
<td>2.50</td>
<td>21.6</td>
<td>0.21</td>
<td>----</td>
<td>Brittle; tears easily</td>
</tr>
<tr>
<td>Membrane</td>
<td>Test Environment</td>
<td>Immer-</td>
<td>Ion Exchange Capacity</td>
<td>H₂O Content</td>
<td>Resistivity</td>
<td>Fe³⁺ Transfer</td>
<td>Physical Condition of Membrane</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>-------</td>
<td>----------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>---------------</td>
<td>---------------------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Time</td>
<td>(meg/dgr)</td>
<td></td>
<td>(meg/cm²)</td>
<td>(mg/cm²/m²)</td>
<td>Burst</td>
<td>Erosion</td>
</tr>
<tr>
<td>103QZL-B2</td>
<td>Dyne1</td>
<td>A</td>
<td>0</td>
<td>2.13</td>
<td>30.1</td>
<td>10.5</td>
<td>22-39</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>2.36</td>
<td>34.2</td>
<td>9.4</td>
<td>15-19</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>2.26</td>
<td>32.0</td>
<td>11.7</td>
<td>10-15</td>
<td>None</td>
</tr>
<tr>
<td>103QZL-B2</td>
<td>Dyne1</td>
<td>B</td>
<td>0</td>
<td>2.45</td>
<td>31.4</td>
<td>9.7</td>
<td>11-37</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>2.46</td>
<td>36.1</td>
<td>9.7</td>
<td>36-100</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>2.34</td>
<td>35.9</td>
<td>10.4</td>
<td>58-97</td>
<td>None</td>
</tr>
<tr>
<td>103QZL-B10</td>
<td>Dynel</td>
<td>A</td>
<td>0</td>
<td>2.24</td>
<td>25.4</td>
<td>10.6</td>
<td>2-3</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>2.59</td>
<td>30.3</td>
<td>9.7</td>
<td>3-4</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>2.34</td>
<td>27.6</td>
<td>14.1</td>
<td>8-10</td>
<td>None</td>
</tr>
<tr>
<td>103QZL-A2</td>
<td>Dynel</td>
<td>A</td>
<td>0</td>
<td>2.98</td>
<td>32.0</td>
<td>6.5</td>
<td>42-68</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>3.11</td>
<td>36.3</td>
<td>7.3</td>
<td>26-45</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>3.52</td>
<td>38.6</td>
<td>7.4</td>
<td>21-56</td>
<td>None</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>Dynel</td>
<td>A</td>
<td>0</td>
<td>3.15</td>
<td>31.6</td>
<td>9.1</td>
<td>1-2</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>3.31</td>
<td>29.8</td>
<td>14.8</td>
<td>4-7</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>3.19</td>
<td>28.8</td>
<td>12.2</td>
<td>5-6</td>
<td>None</td>
</tr>
<tr>
<td>A3L-B7P</td>
<td>Dynel</td>
<td>B</td>
<td>0</td>
<td>3.60</td>
<td>32.2</td>
<td>9.5</td>
<td>1-2</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>3.57</td>
<td>32.4</td>
<td>10.8</td>
<td>3-6</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>3.57</td>
<td>31.7</td>
<td>11.3</td>
<td>7-10</td>
<td>None</td>
</tr>
<tr>
<td>A3L-A5</td>
<td>Dynel</td>
<td>A</td>
<td>0</td>
<td>3.38</td>
<td>32.7</td>
<td>10.1</td>
<td>3-8</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>3.64</td>
<td>34.4</td>
<td>7.8</td>
<td>9-37</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td>3.87</td>
<td>34.5</td>
<td>9.0</td>
<td>72-13</td>
<td>None</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>Dynel</td>
<td>A</td>
<td>0</td>
<td>3.57</td>
<td>35.3</td>
<td>8.7</td>
<td>1-2</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>3.93</td>
<td>32.8</td>
<td>10.6</td>
<td>16-25</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>3.58</td>
<td>32.9</td>
<td>71.4</td>
<td>46-57</td>
<td>None</td>
</tr>
<tr>
<td>Membrane</td>
<td>Test Environment Immersion Time (hrs)</td>
<td>Ion Exchange Capacity (mg/g)</td>
<td>H₂O Content</td>
<td>Resistivity R⁰HSV.NICl (mΩ-cm²)</td>
<td>Fe³⁺ Transfer PFe⁺₃ₓ₁₀⁻³</td>
<td>Physical Condition of Membrane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------</td>
<td>-----------------------------</td>
<td>--------------</td>
<td>---------------------------------</td>
<td>----------------------------</td>
<td>--------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2LD-B2</td>
<td>A</td>
<td>3.72,1.68</td>
<td>93.3</td>
<td>6.9</td>
<td>12-16</td>
<td>None None 132 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teflon</td>
<td>500</td>
<td>3.54,1.68</td>
<td>93.3</td>
<td>6.2</td>
<td>180-220</td>
<td>None None 132 Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness=0.27mm</td>
<td>1000</td>
<td>3.68,1.68</td>
<td>93.3</td>
<td>6.5</td>
<td>Leaks</td>
<td>None None 132 Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2LD-B2</td>
<td>B</td>
<td>3.72,1.68</td>
<td>93.3</td>
<td>6.2</td>
<td>12-16</td>
<td>None None 132 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teflon</td>
<td>100</td>
<td>3.68,1.68</td>
<td>93.3</td>
<td>6.8</td>
<td>24-30</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film Thickness=0.27mm</td>
<td>500</td>
<td>3.51,1.68</td>
<td>93.3</td>
<td>8.3</td>
<td>81-85</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDIL-A5H3</td>
<td>Dyneel</td>
<td>3.93,1.68</td>
<td>93.3</td>
<td>6.9</td>
<td>20-10</td>
<td>None None 145 White, Opaque Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dyneel</td>
<td>100</td>
<td>4.04,1.68</td>
<td>93.3</td>
<td>5.8</td>
<td>8-9</td>
<td>None None 146 White, Opaque Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>4.02,1.68</td>
<td>93.3</td>
<td>6.1</td>
<td>2-10</td>
<td>None None 143 Gray Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDIL-A5H8</td>
<td>Dyneel</td>
<td>3.78,1.68</td>
<td>93.3</td>
<td>7.5</td>
<td>3-36</td>
<td>None None 154 White, Opaque Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dyneel</td>
<td>500</td>
<td>3.92,1.68</td>
<td>93.3</td>
<td>7.0</td>
<td>69-80</td>
<td>None None 154 White, Opaque Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>4.04,1.68</td>
<td>93.3</td>
<td>5.3</td>
<td>28-40</td>
<td>None None 144 White, Opaque Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDIL-A5H10</td>
<td>Dyneel</td>
<td>4.10,1.68</td>
<td>93.3</td>
<td>6.7</td>
<td>5-8</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dyneel</td>
<td>100</td>
<td>4.08,1.68</td>
<td>93.3</td>
<td>5.9</td>
<td>15-25</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.97,1.68</td>
<td>93.3</td>
<td>6.9</td>
<td>34-44</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDIL-A5H10</td>
<td>Dyneel</td>
<td>4.10,1.68</td>
<td>93.3</td>
<td>6.7</td>
<td>5-8</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dyneel</td>
<td>100</td>
<td>4.12,1.68</td>
<td>93.3</td>
<td>6.6</td>
<td>11-13</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.98,1.68</td>
<td>93.3</td>
<td>6.1</td>
<td>3-5</td>
<td>None None 84 Dk. Br. Stiff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDIL-A5-5</td>
<td>A</td>
<td>3.88,1.68</td>
<td>93.3</td>
<td>2.8</td>
<td>5-8</td>
<td>None None 90 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modacrylic</td>
<td>500</td>
<td>3.75,1.68</td>
<td>93.3</td>
<td>2.8</td>
<td>24-43</td>
<td>None None 90 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness=0.12mm</td>
<td>1000</td>
<td>3.70,1.68</td>
<td>93.3</td>
<td>3.0</td>
<td>12-15</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDIL-A5-5</td>
<td>B</td>
<td>3.88,1.68</td>
<td>93.3</td>
<td>2.8</td>
<td>5-8</td>
<td>None None 90 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modacrylic</td>
<td>250</td>
<td>4.02,1.68</td>
<td>93.3</td>
<td>3.2</td>
<td>77-81</td>
<td>None None 90 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness=0.012mm</td>
<td>500</td>
<td>3.90,1.68</td>
<td>93.3</td>
<td>4.3</td>
<td>~2000</td>
<td>None None 90 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>3.62,1.68</td>
<td>93.3</td>
<td>2.3</td>
<td>Leaks</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP4L-A2</td>
<td>A</td>
<td>5.30,2.94</td>
<td>93.3</td>
<td>1.8</td>
<td>4-8</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modacrylic</td>
<td>100</td>
<td>4.96,2.69</td>
<td>93.3</td>
<td>1.9</td>
<td>2-8</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness=0.025mm</td>
<td>1000</td>
<td>5.16,2.97</td>
<td>93.3</td>
<td>1.8</td>
<td>10-16</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP4L-A2</td>
<td>B</td>
<td>5.30,2.94</td>
<td>93.3</td>
<td>1.8</td>
<td>4-8</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film Thickness=0.025mm</td>
<td>1000</td>
<td>5.26,2.94</td>
<td>93.3</td>
<td>1.1</td>
<td>6-9</td>
<td>None None 84 None Flexible</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TABLE 12. CONTINUED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Membrane Sample Size - $45 \text{ cm}^2$ (dia=7.6cm)

Membrane Sample Thickness: 0.55-0.60 cm except where noted
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Film Thickness (mm)</th>
<th>Backing Fabric</th>
<th>Area Resistivity $R^0$, LN HCl, (Ω-cm$^2$)</th>
<th>Resistance Ratio R0.1/R6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>103QZL-B2</td>
<td>0.60</td>
<td>Dynel</td>
<td>11.1 6.80 4.17 3.03 2.06</td>
<td>6.4</td>
</tr>
<tr>
<td>103QZL-10</td>
<td>0.60</td>
<td>Dynel</td>
<td>15.4 9.6 6.40 4.16 3.26</td>
<td>4.7</td>
</tr>
<tr>
<td>103QZL-10</td>
<td>0.27</td>
<td>Teflon</td>
<td>6.81 4.24 2.63 1.55 1.43</td>
<td>4.6</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>0.60</td>
<td>Dynel</td>
<td>15.4 10.0 6.45 5.28 3.26</td>
<td>4.7</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>0.27</td>
<td>Teflon</td>
<td>8.50 5.55 3.75 2.23 1.95</td>
<td>4.6</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>0.15</td>
<td>Polypropylene</td>
<td>11.99 ---- 3.17 ---- ----</td>
<td>---</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>0.25</td>
<td>Polypropylene</td>
<td>9.04 ---- 3.66 ---- ----</td>
<td>---</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>0.60</td>
<td>Dynel 183</td>
<td>12.0 10.1 7.72 6.43 3.54</td>
<td>3.4</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>0.27</td>
<td>Teflon</td>
<td>6.53 5.17 4.19 3.03 2.03</td>
<td>3.1</td>
</tr>
<tr>
<td>CD1L-A5H-10</td>
<td>0.60</td>
<td>Dynel</td>
<td>6.80 5.75 4.19 3.79 2.96</td>
<td>2.3</td>
</tr>
<tr>
<td>CD1L-A5H-10</td>
<td>0.11</td>
<td>Modacrylic</td>
<td>3.75 3.00 2.50 2.15 1.58</td>
<td>2.4</td>
</tr>
<tr>
<td>CD1L-A5H-10</td>
<td>0.23</td>
<td>Modacrylic</td>
<td>2.39 2.50 2.15 1.80 1.61</td>
<td>1.5</td>
</tr>
<tr>
<td>Solution Resistance (ohms)</td>
<td></td>
<td></td>
<td>10.9 3.2 2.10 1.68 1.37</td>
<td>8.0</td>
</tr>
</tbody>
</table>
# TABLE 14

MEMBRANE RESISTIVITY AS A FUNCTION OF NaCl CONCENTRATION

Method of Measuring Liquid Junction
Cell Cross Sectional Area = 1.36 cm²
Meas. Frequency - 1000 Hz
Temp = 25°C

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Membrane Thickness (mm)</th>
<th>Area Resistivity</th>
<th>Resistance Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( R^* ), LN NaCl (ohm·cm²)</td>
<td>0.1</td>
</tr>
<tr>
<td>103QZL-B2</td>
<td>0.60</td>
<td>12.3 11.5 9.28 7.39 5.64</td>
<td>2.2</td>
</tr>
<tr>
<td>103QZL-B10</td>
<td>0.60</td>
<td>16.2 14.4 12.3 10.5 8.61</td>
<td>1.9</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>0.60</td>
<td>15.9 14.4 12.5 10.9 8.87</td>
<td>1.8</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>0.60</td>
<td>11.3 11.2 10.2 9.06 9.36</td>
<td>1.4</td>
</tr>
<tr>
<td>CDL-ASH-10</td>
<td>0.60</td>
<td>6.20 6.66 6.26 5.89 5.90</td>
<td>1.05</td>
</tr>
<tr>
<td>CDL-A5-3</td>
<td>0.11</td>
<td>3.67 3.64 3.44 3.34 3.60</td>
<td>1.08</td>
</tr>
<tr>
<td>CP4L-A2</td>
<td>0.23</td>
<td>2.18 2.58 2.77 2.60 3.47</td>
<td>0.63</td>
</tr>
<tr>
<td>Solution Resistance (ohms)</td>
<td>28.3 8.82 5.41 3.64 2.68</td>
<td>10.6</td>
<td></td>
</tr>
</tbody>
</table>

56
<table>
<thead>
<tr>
<th>Membrane (Electrolyte)</th>
<th>Specific Resistivity $\rho^j$ at 25°C ((\Omega\cdot\text{cm})) at Electrolyte Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1N</td>
</tr>
<tr>
<td>103QZL-B2</td>
<td>218</td>
</tr>
<tr>
<td>103QZL-B10</td>
<td>257</td>
</tr>
<tr>
<td>A3I-7</td>
<td>257</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>200</td>
</tr>
<tr>
<td>CD1LA5H10</td>
<td>113</td>
</tr>
<tr>
<td>CD1LA5-3</td>
<td>341</td>
</tr>
<tr>
<td>CP4L-A2</td>
<td>104</td>
</tr>
<tr>
<td>(HCl)</td>
<td>26.3</td>
</tr>
</tbody>
</table>

Measurement by liquid junction method at 25°C

HCl Conductivity Data - International Critical Tables Vol. VI, 1929
### TABLE 16.

**SPECIFIC RESISTANCE OF CANDIDATE MEMBRANES IN NaCl**

<table>
<thead>
<tr>
<th>Membrane (Electrolyte)</th>
<th>Specific Resistivity, $\rho$ at 25°C (Ω-cm)</th>
<th>at Electrolyte Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1N</td>
<td>0.5N</td>
</tr>
<tr>
<td>103Q2L-B2</td>
<td>205</td>
<td>192</td>
</tr>
<tr>
<td>103Q2L-B10</td>
<td>270</td>
<td>240</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>270</td>
<td>240</td>
</tr>
<tr>
<td>B2LDT-B2</td>
<td>188</td>
<td>187</td>
</tr>
<tr>
<td>D1L-A5H10</td>
<td>103</td>
<td>111</td>
</tr>
<tr>
<td>CD1L-A5-3</td>
<td>352</td>
<td>331</td>
</tr>
<tr>
<td>CP4L-A2-2</td>
<td>95</td>
<td>112</td>
</tr>
<tr>
<td>(NaCl)</td>
<td>33.7</td>
<td>21.3</td>
</tr>
</tbody>
</table>

NaCl solutions acidified to 0.01N in HCl to activate weak base amines.

Measurement by liquid junction method at 25°C.

NaCl Conductivity Data - Robinson R. A. and Stokes RH, Electrolyte Solutions, 2nd ed. 1959 p.466

-and International Critical Tables, Vol. VI-1929
### TABLE 17.

**Fe TRANSFER IN ANION MEMBRANES AS A FUNCTION OF FeCl$_3$ CONCENTRATION**

All FeCl$_3$ Solutions 1.0K in HCl

Current Density - 60ma/cm$^2$

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Film Thickness (mm)</th>
<th>Fe Transfer $P$$_{Fe}$ (mgFe/mF x 10$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5M FeCl$_3$</td>
</tr>
<tr>
<td>103QZL-B2</td>
<td>0.60</td>
<td>18-30</td>
</tr>
<tr>
<td>103QZL-B10</td>
<td>0.60</td>
<td>3-4</td>
</tr>
<tr>
<td>CD1L A5H-10</td>
<td>0.60</td>
<td>3</td>
</tr>
<tr>
<td>CP4L-A2-2</td>
<td>0.23</td>
<td>3-4</td>
</tr>
<tr>
<td>CD12-A5</td>
<td>0.11</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table 18.

**Fe\(^{+3}\) Transfer as a Function of Current Density**

Test Electrolyte - 2M Fe Cl\(_3\)/1N HCl  
Temp. Ambient - Electrolyte Flow = 1.5 cm/sec

<table>
<thead>
<tr>
<th>Current Density (mA/cm(^2))</th>
<th>Fe(^{+3}) Transfer, (P_{Fe}^{+}) (mgFe/m²x10(^{-3})) for Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>103Q2L-2198 4.1-5.3x10(^3)</td>
</tr>
<tr>
<td>30</td>
<td>3.4-4.4x10(^3) 2.7-3.2x10(^3)</td>
</tr>
<tr>
<td>60</td>
<td>1.1-1.2x10(^3) 1.1-1.2x10(^3)</td>
</tr>
<tr>
<td>120</td>
<td>84-99 7-13(9)</td>
</tr>
<tr>
<td>480</td>
<td>7-13</td>
</tr>
</tbody>
</table>
**TABLE 19.**

**SUMMARY PROPERTIES OF PRODUCTION SCALE CANDIDATE MEMBRANES**

- Size of individual sheet - 20"x42" (5.8 ft²)
- Backing - Dyneel
- No. samples analyzed = 15

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Sheets Manufactured</th>
<th>Total area Prod.</th>
<th>IEC (meq/dgr)</th>
<th>H₂O</th>
<th>Elec. Resis. Rₚ in 0.1N HCl (ohm-cm²)</th>
<th>Thickness (mm)</th>
<th>Burst Strength (psi)</th>
<th>Physical Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>103QZL-B2</td>
<td>6</td>
<td>34 ft² (3.16 m²)</td>
<td>2.3-2.6</td>
<td>31.1-31.6</td>
<td>7.9-9.7</td>
<td>0.58-0.60</td>
<td>129-150</td>
<td>No leaks, well coated, uniform</td>
</tr>
<tr>
<td>A3L-B7</td>
<td>10</td>
<td>60 ft² (5.57 m²)</td>
<td>3.4-3.8</td>
<td>30.8-33.5</td>
<td>9.1-10.3</td>
<td>0.53-0.59</td>
<td>136-154</td>
<td>3 pinholes, well coated, uniform</td>
</tr>
<tr>
<td>Membrane</td>
<td>Sample</td>
<td>Burst psi</td>
<td>Thickness (mm)</td>
<td>$R_c^{0.1N}$ HCl</td>
<td>$R_c^{0.01}$ NaCl</td>
<td>IEC</td>
<td>%H₂O</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
<td>-----------</td>
<td>----------------</td>
<td>------------------</td>
<td>------------------</td>
<td>-----</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>141</td>
<td>0.58, 0.58, 0.58</td>
<td>9.7</td>
<td>15.0</td>
<td>2.53</td>
<td>31.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>134</td>
<td>0.58, 0.58, 0.58</td>
<td>9.1</td>
<td>15.0</td>
<td>2.50</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>139</td>
<td>0.58, 0.58, 0.58</td>
<td>9.4</td>
<td>15.0</td>
<td>2.54</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>129</td>
<td>0.58, 0.58, 0.59</td>
<td>8.4</td>
<td>15.5</td>
<td>2.45</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>130</td>
<td>0.58, 0.60, 0.60</td>
<td>9.3</td>
<td>15.4</td>
<td>2.52</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>139</td>
<td>0.59, 0.59, 0.59</td>
<td>8.1</td>
<td>15.3</td>
<td>2.57</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>146</td>
<td>0.59, 0.59, 0.60</td>
<td>8.5</td>
<td>15.5</td>
<td>2.56</td>
<td>31.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>150</td>
<td>0.58, 0.59, 0.58</td>
<td>8.4</td>
<td>15.2</td>
<td>2.34</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>143</td>
<td>0.60, 0.60, 0.60</td>
<td>8.4</td>
<td>15.0</td>
<td>2.33</td>
<td>31.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>144</td>
<td>0.58, 0.58, 0.59</td>
<td>8.5</td>
<td>15.5</td>
<td>2.42</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>140</td>
<td>0.60, 0.60, 0.60</td>
<td>7.9</td>
<td>15.5</td>
<td>2.47</td>
<td>31.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>139</td>
<td>0.59, 0.59, 0.59</td>
<td>8.5</td>
<td>15.1</td>
<td>2.41</td>
<td>31.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>150</td>
<td>0.60, 0.59, 0.59</td>
<td>8.6</td>
<td>15.4</td>
<td>2.43</td>
<td>31.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>142</td>
<td>0.59, 0.59, 0.59</td>
<td>8.7</td>
<td>15.5</td>
<td>2.46</td>
<td>31.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>137</td>
<td>0.59, 0.59, 0.59</td>
<td>8.9</td>
<td>15.0</td>
<td>2.40</td>
<td>31.4</td>
<td></td>
</tr>
</tbody>
</table>
## Table 21.

### Properties - Samples from Production Scale Membranes

**No. Manufactured:** 10

**Size of Membrane Sheet:** 20" x 42"

#### A3L-B7P Membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Sample</th>
<th>Burst (psi)</th>
<th>Thickness (mm)</th>
<th>$R^c_{0.1NHCL}$ (cm$^2$)</th>
<th>IEC (mg/dgr)</th>
<th>%H$O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>143</td>
<td>.54,.55,.54</td>
<td>10.4</td>
<td>3.59</td>
<td>34.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>142</td>
<td>.53,.54,.54</td>
<td>9.4</td>
<td>3.45</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>148</td>
<td>.56,.56,.56</td>
<td>9.1</td>
<td>3.57</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>143</td>
<td>.53,.54,.55</td>
<td>9.2</td>
<td>3.66</td>
<td>33.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>136</td>
<td>.55,.55,.54</td>
<td>9.7</td>
<td>3.79</td>
<td>33.4</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>143</td>
<td>.54,.55,.55</td>
<td>10.3</td>
<td>3.61</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>147</td>
<td>.57,.57,.57</td>
<td>10.0</td>
<td>3.54</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>145</td>
<td>.54,.54,.54</td>
<td>10.6</td>
<td>3.48</td>
<td>31.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>153</td>
<td>.56,.56,.55</td>
<td>10.0</td>
<td>3.51</td>
<td>31.1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>148</td>
<td>.57,.57,.57</td>
<td>10.6</td>
<td>3.40</td>
<td>32.1</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>148</td>
<td>.55,.55,.56</td>
<td>9.7</td>
<td>3.59</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>142</td>
<td>.57,.58,.58</td>
<td>9.6</td>
<td>3.39</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>141</td>
<td>.57,.57,.58</td>
<td>9.8</td>
<td>3.40</td>
<td>31.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>154</td>
<td>.59,.59,.58</td>
<td>9.4</td>
<td>3.41</td>
<td>30.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>141</td>
<td>.55,.55,.56</td>
<td>9.1</td>
<td>3.65</td>
<td>31.1</td>
</tr>
</tbody>
</table>
### TABLE 22.

**STATISTICAL ANALYSIS - STANDARD AND CANDIDATE MEMBRANES**

<table>
<thead>
<tr>
<th>MEMBRANE</th>
<th>ION EXCHANGE CAPACITY</th>
<th>WATER CONTENT</th>
<th>FILM THICKNESS (mm)</th>
<th>RESISTIVITY (n-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IEC (meq/dgr)</td>
<td>H₂O (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>X ±3σ% Range</td>
<td>X ±3σ% Range</td>
<td>X ±3σ% Range</td>
<td>X ±3σ% Range</td>
</tr>
<tr>
<td>T03Q2L-B2P</td>
<td>2.46 ±0.23 ±9.3 % 2.23-2.69</td>
<td>31.3 ±0.6 ±1.9 30.7-31.9</td>
<td>0.59 ±0.034 ±5.8 0.56-0.62</td>
<td>8.7 ±1.3 ±13.8 7.5-9.8</td>
</tr>
<tr>
<td>A3L-B7P</td>
<td>3.54 ±0.61 ±17.2 ±2.93-3.69</td>
<td>32.5 ±3.7 ±11.4 28.8-33.2</td>
<td>0.56 ±0.050 ±8.9 ±0.51-0.61</td>
<td>9.8 ±1.7 ±17.3 ±8.1-11.0</td>
</tr>
</tbody>
</table>

**Key:**
- $\bar{X}$ = Average of samples analyzed
- $+3\sigma$ = 3 sigma variance
- $\%$ = Variance percent, $3\sigma$
Figure 1. Polymer Structure - Candidate Anion Membranes

a. 103QZL - divinylbenzene, vinylbenzylchloride copolymer aminated with trimethylamine

b. A3L - divinylbenzene, 2-vinylpyridine copolymer

c. BZLDT - divinylbenzene, vinylbenzylchloride copolymer aminated with diethylene triamine
Figure 1. Polymer Structure - Candidate Anion Membranes (Cont.)

d. **CDIL** - vinylbenzylchloride, dimethylaminoethylmethacrylate copolymer

\[
\begin{align*}
\text{CDIL - vinylbenzylchloride, dimethylaminoethylmethacrylate copolymer} & \\
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\text{CDIL - vinylbenzylchloride, dimethylaminoethylmethacrylate copolymer}
\]

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site

\[
\begin{align*}
\text{CH}_3 & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{N} & \\
\downarrow & \\
\text{CH} & \\
\downarrow & \\
\text{CH}_2 & \\
\downarrow & \\
\text{CH}_3 & \\
\downarrow & \\
\text{Cl} & \\
\end{align*}
\]

Quaternary Site

Tertiary Site
Figure 2. POLYMER STRUCTURE - ALTERNATIVE SYSTEMS

a. CT - vinylbenzylchloride and tetraethylenepentamine (TEPA) copolymer

\[
\begin{align*}
&\text{CH}_2\text{CH}_n \quad \text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{NH}_2\text{CH}_2\text{NH}_2\text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{NH}_2\text{Cl}^- \\
&\text{Cl}^- \\
&\text{CH}_2\text{CH}_n
\end{align*}
\]

b. CTM - vinylbenzylchloride and N, N, N', N' tetramethylethylenediamine (TMEDA) copolymer

\[
\begin{align*}
&\text{CH}_2\text{CH}_n \\
&\text{CH}_3\text{Cl}^- \\
&\text{CH}_3\text{Cl}^- \\
&\text{CH}_3\text{Cl}^- \\
&\text{CH}_3\text{Cl}^- \\
&\text{CH}_2\text{CH}_n
\end{align*}
\]

c. VC-TP - polyvinylchloride film aminated with tetraethylenepentamine (TEPA)

\[
\begin{align*}
&\text{CH}_2\text{CH}_n \quad \text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{NH}_2\text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{NH}_2\text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{NH}_2\text{Cl}^- \\
&\text{CH}_2\text{CH}_2\text{NH}_2\text{Cl}^- \\
&\text{Cl}^- \\
&\text{CH}_2\text{CH}_n
\end{align*}
\]
Figure 2. (Cont.) POLYMER STRUCTURE - ALTERNATIVE SYSTEMS

d. CE - vinylbenzylchloride-ethylenediamine (EDA) copolymer

![Chemical Structure](CE.png)

\[ \text{(-CH}_2\text{CH}_2\text{)}_n \]

\[ \text{CH}_2\text{NH}_2\text{CH}_2\text{NH}_2\text{CH}_2 \]

\[ \text{(-CH}_2\text{CH}_2\text{)}_n \]

e. CD - vinylbenzyl chloride and diethylenetriamine (DETA) copolymer

![Chemical Structure](CD.png)

\[ \text{(-CH}_2\text{CH}_2\text{)}_n \]

\[ \text{CH}_2\text{NH}_2\text{CH}_2\text{NH}_2\text{CH}_2 \]

\[ \text{(-CH}_2\text{CH}_2\text{)}_n \]

f. CX - 4-vinyl pyridine (4-VP) and \( \alpha \alpha' \) dichlоро p-xylene copolymer

![Chemical Structure](CX.png)

\[ \text{(-CH}_2\text{CH}_2\text{)}_n \]

\[ \text{CH}_2\text{NH}_2\text{CH}_2\text{NH}_2\text{CH}_2 \]

\[ \text{(-CH}_2\text{CH}_2\text{)}_n \]
Figure 2. (cont.) POLYMER STRUCTURE - ALTERNATIVE SYSTEMS

g. SEM - sulfoethylmethacrylate and ethyleneglycoldimethacrylate copolymer

\[
\begin{align*}
&\text{CH}_3 & \text{CH}_3 \\
&\text{CH} & \text{CH} \\
&\text{O} & \text{SO}_3^- \\
&\text{CH}_2 & \text{CH}_2 \\
&\text{CH}_2 & \text{CH}_2 \\
&\text{O} & \text{H}^+ \\
&\text{CH}_2 & \text{CH}_2 \\
&\text{CH}_3 & \text{CH}_3
\end{align*}
\]
FIGURE 3

Membrane Resistivity, $R^j$, as a function of HCl Concentration at 25°C

103QZL-B2 Membrane

- □ - Dynel Backing  Film Gage-0.60mm

103QZL-B10

- ○ - Dynel backing  Film Gage-0.60mm
- △ - Teflon backing  Film Gage-0.27mm

ORIGINAL PAGE IS OF POOR QUALITY
FIGURE 4.
Membrane Resistivity, $R_\phi$, as a Function of HCl Concentration at 25°C

A3L-B7 Membrane
- O Dynel Backing  Film Gage-0.60mm
- △ Teflon Backing Film Gage-0.27mm
- □ Polypropylene Backing Film Gage-0.25mm

HCl Concentration (N)
FIGURE 5.
Membrane Resistivity, $R_a^j$, as a Function of HCl Concentration at 25°C

B2LDT-B2 Membranes
- O Dynel Backing
- △ Teflon Backing

HCl Concentration (N)
Figure 6. Membrane resistivity, $R_J$, as a function of HCl concentration at 25°C.

- **CDU-A5 Membrane**
  - O Dynel Backing, Film Gage-0.60mm
  - △ Modacrylic Backing, Film Gage-0.11mm

- **CP4L-A2**
  - △ Modacrylic Backing

The original page is of poor quality.
Figure 7: Fe Transfer ($\text{Fe}^{2+}$) in Anion Selective Membranes as a Function of Current Density

Membranes: ○ 103Q2L-219S; □ A3L-A5, △ A3L-A6
Test soln. 2M FeC13/1M HCl, Cell polarity - charge mode
Test soln. Flow = 1.5 cm/sec.