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Advances in Membrane Technology for the NASA Redox Energy Storage System

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ENERGY STORAGE SYSTEM

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SUMMARY

Anion exchange membranes used in the NASA Redox energy storage system based on the soluble iron and chromium chloride redox couples, have been under development by Ionics, Inc. of Watertown, Massachusetts, for the past 5 years. The CDIL series (a copolymer of vinylbenzyl-chloride and dimethyl-aminoethyl methacrylate), has demonstrated superior properties in the Redox environment. Recent improvements in the area - resistivity and ion selectivity have resulted from minor variations in this membrane formulation. Resistivities at several acid and iron solution concentration, iron diffusion rates, and time-dependent iron fouling of the various membrane formulations will be presented.

A brief section on Redox membrane technology is included. Discussed in this section are basic membrane principles and requirements, characteristics which may be varied to optimize membrane properties, and surface fouling phenomenon caused by exposure to complexed iron ions.

Experimental screening tests for the determination of membrane characteristics include procedures for pinhole detection, ferric ion fouling, ion selectivity, area resistivity, and cell performance. From these tests, tables of results were compiled which led to the choice of the present standard; CDIL-AA5-0.0625 catalyst membrane for the NASA-Redox Energy Storage System.

The optimized CDIL membrane shows a marked resistance to the surface fouling effect seen in past membranes. Minor formula variations were incorporated into this membrane allowing a cell performance twice that of previous membrane formulations. The characteristics of this membrane are as follows: Thickness = 0.035 - 0.040 cm, water content = 39 - 42 percent, Selectivity = 20 $\mu\text{g Fe/nr/cm}^2\text{/M/L}$, Area resistivity ($\omega - \text{cm}^2$) = 3.6 in 1.0 N HCl, 3.9 in 0.5 M Fe^{+3} , 5.4 in 1.0 M Fe^{+3} , and 10.3 in 1.5 M Fe^{+3} . (All iron solutions used in resistivity tests contained HCl at a concentration of 1.0 N.) There is a slight Fe^{+3} fouling effect, much decreased from past formulations, and, consequently, better resistance stability with time.

INTRODUCTION

In 1974 the concept of an electrochemical storage system based on two fully soluble Redox couples separated by an ion exchange membrane was presented at the ninth IECEC meeting (ref. 1). In conceptual form, the use of tanks to store Redox fluids and pumps to circulate the stored reactants through the stack of individual Redox flow cells was described. The potential advantages of this concept, in which the storage portion of the overall system can be sized independently of the power-related portion of the system and in which no solid electrode reactants are present, were outlined.

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Membrane studies and a search to find an appropriate separator for the Redox flow cell also began at this time. For the past 5 years the NASA Lewis Research Center has been conducting screening experiments (refs. 2 to 4) of anion exchange membranes developed under contract (refs. 5 and 6) by Ionics, Inc. of Watertown, Massachusetts, for the NASA-Redox Energy Storage System. Briefly, this energy storage system basically consists of two reactant solutions (at present 1.0 M CrCl_3 and 1.0 M FeCl_2 each in 2.0 N HCl), circulated through a multi-cell power conversion unit called a stack (ref. 7). The membrane serves as a charge transferring medium as well as a reactant separator and is one of the key enabling components in this storage technology.

This paper will cover the membrane properties and recent technology advances made on the anion exchange membranes required for the NASA-Redox Energy Storage System. The purpose of this work is to develop membranes for Redox energy storage systems for solar photovoltaic and utility load leveling applications. Characteristics to be discussed are reactant crossmixing, ionic conductivity, long-term resistance stability, and cell performance of experimental membranes developed during the past several years.

REDOX MEMBRANE TECHNOLOGY

Principles

Ion selective membranes are electrically conductive due to the fixed ionized sites incorporated in the polymer matrix. This permits movement of the mobile counter ions in the electrolyte solution. The separation of the two electrolytes (iron chloride and chromium chloride) is controlled by the Donnan principle in excluding the co-ions from the membrane phase (ref. 8). Electrolyte exclusion is, in general, supported by high ion exchange capacity and low porosity of polymer resin. Electrolyte exclusion is also favored in dilute electrolyte concentration, low valence state of counter ions, and high valence of the co-ions. The membranes that are most selective are those which succeed in excluding highly concentrated electrolytes.

Different polymer resins absorb varying amounts of electrolyte (Donnan diffusion, ref. 8) depending on their physical and chemical properties and the nature and composition of the electrolyte solutions. Membrane resistivity measured in solution indicates the additive mobilities of the counter ions (Cl^-) and the absorbed electrolyte (HCl), and is dependent on: (1) the ion exchange capacity, (2) the counter ion mobility associated with a particular ion exchange site, and (3) the mobility of the co-ions which diffuse into the pore structures of the membrane. The ionic species in acidified ferric chloride solutions include Fe^{+3} , H^+ , Cl^- and the complex ions FeCl_2^+ , FeCl^{+2} , FeCl_4^- , and FeCl_6^{3-} at varying concentrations depending on the acidity of the solution (refs. 5 and 6).

Figure 1 represents a simple cross diffusion model of the Redox system. The general equation governing anion exchange membrane cross diffusion is as follows:

$$\text{Cross diffusion} = (\text{constant}) \times (\text{area}) \times (\text{time}) \times (\text{driving force})$$

In the Redox system cross diffusion leads to a reduction in capacity due to loss of the reactant being present in its initial solution. If a highly selective membrane is utilized, this reduction in capacity is minimized. In general, capacity loss is a function of (membrane characteristics) x (some

measurable parameters). The measurable parameters mentioned here are those listed in the cross diffusion equation (i.e., area, time, driving force, and a constant).

Requirements

Considering the principles just mentioned, a series of properties required of a membrane for use in the Redox Energy Storage System can be listed along with other important properties not pertaining to the principles discussed above. Physical and electrochemical properties essential for viable Redox cell operation are as follows:

- o High counter ion conductivity (Cl-counter ion)
- o High selectivity - minimum transfer of iron and chromium reactant solutions
- o Low electrical area resistivity and high resistivity stability - allows high power output
- o Durability when exposed to Redox environment at various temperatures - early membranes failed structurally at high temperatures resulting in a great loss of selectivity
- o Capability for scaled-up manufacturing - in order for mass production of Redox systems to be feasible, membranes must be made larger and in greater quantity

Characteristics

The CDIL series of membranes (a copolymer of vinylbenzyl chloride and dimethylaminoethyl methacrylate) has, by virtue of its chemical stability and high ion exchange capacity, demonstrated superior properties in the Redox environment. Improvements made within the last year by Ionics, Inc. have resulted from minor variations in the membrane formulation. Within any particular membrane chemistry minor changes can be made which have a profound effect on the resultant properties. There are four main constituents which easily lend themselves to controlled variation:

1. Non-polymerizable material or solvent (NP content) - As the fraction of NP material increases, the membrane structure is made more open by enlarging the pore sizes. If pore size is increased, ions can pass through at a faster rate and resistivity is likely to be lower. If the pore size is allowed to be too large, however, the ionic species that should be kept separate will crossmix. In a Redox system this results in a loss of storage capacity. Conversely, if pore size is decreased (indicating a decrease in NP content), membrane resistance will increase. However, a trade-off situation exists between the membrane selectivity, pore size, and resistivity. Pore size is one of the factors which controls resistivity and selectivity. Pores must be small enough to hinder the passage of large metal cations and yet allow the passage of the chloride ions. (The considerably smaller hydrogen ions are too small to be excluded.) Pores must also be large enough for an acceptable area resistivity. These factors are inversely related which suggests that an optimum pore size exists.

2. Catalyst level - Variation of the polymerizing catalyst controls the polymerization rate. Reducing its concentration slows the formation of undesirable high viscosity monomer adducts, until an optimum level is attained.

3. Crosslinker density and type - (a) The vinylbenzyl chloride crosslink monomer forms (with backbone of dimethylaminoethyl methacrylate in the

polymerized CDIL film) a quaternary adduct resulting in the high crosslink density of the copolymers. Concentration ratio variations of the two monomers can produce different properties. (b) Substitution of one crosslinking monomer for another can also result in different properties.

4. Membrane thickness - A reduction in membrane thickness should decrease membrane resistivity without changing the selectivity. This can be done by decreasing substrate (fabric backing) thickness.

Surface Fouling

In tests conducted at both Ionics, Inc. (ref. 6) and NASA Lewis (ref. 4) it was discovered that in ferric chloride solutions acidified with HCl, where negative complex Fe^{+3} ions were present, membranes required longer exposure to the $FeCl_3$ solution in order to reach a stable area resistivity. Some membranes never reached a stable resistivity value, and continued to increase, rendering them unusable. The anion membranes, in acid environments considered weak or dilute (0.5 to 1.0 N HCl), apparently behaved as ion scavengers removing the negative complex ions as they formed until the active polymer sites were used up. This would indicate that anion membranes are susceptible to large increases in resistance in a $FeCl_3$ environment of acidity 0.5 N and higher.

The primary aim of this work was to reduce the membrane's sensitivity to Fe^{+3} through minor variations in the CDIL chemistry, while maintaining acceptable reactant selectivity.

Experimental Screening Tests

Each membrane formulation undergoes a series of screening tests to determine whether or not it is suitable for use in a Redox system. All membrane samples received are subjected to the following tests:

1. Dye testing for pinholes - Membranes are placed on dampened absorbent paper (membranes must be kept wet at all times). Methylene blue dye solution is then applied to the surface of the membrane and distributed evenly by hand, with light to moderate pressure. The entire surface is treated in this manner except for a 1/2-inch margin around the membrane's edge. This is to avoid an erroneous indication of a pinhole. If dye appears on the absorbent paper beneath the membrane, that area is tested again. Upon confirmation of a pinhole and its location, the membrane is wiped dry, pinholes are quickly marked, and the membrane is placed into DI water.

2. Static diffusion/selectivity tests - Small samples of membrane material are placed in the apparatus shown in figure 2. One cavity is filled with 1.0 M $FeCl_3$ made with 0.5 N HCl and the other cavity is filled with 0.5 N HCl. After 24 hours, the acid is withdrawn with a syringe, diluted to 50 cm^3 with 0.5 N HCl, and analyzed for total Fe^{+3} content. For extended testing, fresh 0.5 N HCl is replaced and the exposure time increased. Sampling and analysis are then repeated as before.

3. Resistivity flow tests for area resistivity stability in different $FeCl_3$ concentrations - A flow cell is assembled with an inert iron electrode made of carbon felt (ref. 7) on each side of the membrane. Figure 3 is a schematic representation of this setup. Resistivity measurements are taken and data is plotted with respect to time to determine resistance increase and stability. A "blank" correction is made for the resistance contribution of the cell current collectors and electrodes.

The following tests are performed on selected membrane samples that pass the above mentioned screening tests:

1. Area resistivity in various solutions at various temperatures (25° to 50° C) - Membrane samples are soaked in glass containers with various concentrations of iron solutions and placed in ovens stabilized at a certain temperature. At predetermined intervals of time, individual samples are removed, placed between two half cells, and tested for resistivity. The sample is then placed back into its container and returned to the oven for the next time period.

2. Selectivity in various solutions at various temperatures (25° to 50° C) - The selectivity apparatus shown in figure 2 is placed in a humidified chamber, transferred to an oven, and allowed to stabilize at the desired temperature. Selectivity is determined in the same manner as above.

3. Performance in Redox cells using various solutions at several concentrations and operating temperatures (selectivity and resistivity versus time are included in this test) - Lab-size cells (14.5 cm²) are used to test membranes under charge/discharge conditions. Polarization tests are used to compare cell performance using 1.0 M and 1.5 M iron solutions. Membrane resistance is also measured as a function of cycling time. A description of the testing system is given in reference 2.

This range of testing seems to give a clear understanding of the behavior a membrane will exhibit when introduced to a Redox environment. From this kind of data, valid predictions of the maximum selectivity and final resistivity can be made enabling accurate calculations of power density and sizing of Redox systems.

RESULTS AND DISCUSSION

Surface Fouling

The surface fouling phenomenon is more clearly understood through a series of resistance tests. Membrane soak tests were used to relate resistivity increase to time of exposure and state of charge. This phenomenon was investigated as follows. Small samples of membranes were soaked in different concentration ratios of ferrous and ferric chloride solutions, thus simulating several states of charge in the iron solution. Resistance measurements were obtained at different time intervals. Figure 4 indicates that the resistance increase was due to the ferric ion solution and is a function of its concentration. Ferrous ion and hydrochloric acid solutions show no resistance increase. Ferric ions form negative complex ions which interact at the membrane surface producing ferric ion fouling. When soaked in dilute hydrochloric acid, a "fouled" membrane will return to its original resistance, indicating that the fouling effect is reversible. In another test, membrane samples were soaked in Fe₂(NO₃)₃ solutions. In the presence of nitrate ion, Fe III has little tendency to form complex ions, thus the predominant species is Fe⁺³. The results are shown in figure 5. Membrane resistance in the presence of the nitrate ion was stable until chloride ion was added to the solution and ferric chloro complexes are formed. It is thus concluded that the membrane fouling is due to ferric ion complexes. Chromium solutions appear to have no fouling effect.

CDIL Membrane Optimization Techniques

Experiments were conducted varying the CDIL chemistry in an attempt to decrease membrane sensitivity to ferric ion fouling and thus produce a low resistivity membrane having good selectivity.

Minor variations were made in the basic formulation of the standard CDIL chemistry by altering the NP content, the catalyst level, and the crosslink density and type. Table I contains a sampling of the various alterations. The resistivity of each membrane in various HCl/Fe solution combinations are presented along with the selectivity in 1 M FeCl₃/0.5 N HCl. The resistance stability in the presence of FeCl₃ solutions for some of the variations are shown in figure 6. The effect of these variations are discussed below.

NP Content

The effect of variation of the NP content can be seen by comparing the past standard membrane having a 25-NP content with a similar CDIL membrane with a 20-NP content. The selectivity of the 20 NP content was much better than the 25 NP content ($7 \mu\text{g Fe/hr/cm}^2$ versus $15 \mu\text{g Fe/hr/cm}^2$, respectively). However, the 20 NP membrane had a considerably higher resistivity value. Both the selectivity and the resistivity are influenced by the NP content which is the main parameter affecting membrane pore sizes. In general, the higher the NP content, the larger the pore size will be within a membrane, thus leading to a less selective but lower resistivity membrane. A second example of the effect of NP content variation is shown in figure 7. The selectivities of two CDIL membranes (25 and 35 NP) and two CP4L membranes (35 and 40 NP) with chromium are compared as a function of chromium concentration. The figure illustrates the relation between pore size, chromium concentration, and diffusion rate. The "tight" membranes (lower NP, smaller pore size) retain their selective properties even at higher chromium concentrations, but above 1.8 M the higher NP membranes lose selectivity rapidly.

Using selectivity data of this kind, an estimate of capacity loss in a Redox system can be made since cross diffusion is responsible for capacity loss. Figure 8 illustrates the relationship of capacity loss as a function of time for a membrane with a $20 \mu\text{g Fe/hr/cm}^3/\text{M/L}$ diffusion parameter. In a period of approximately 30 years a capacity loss of 25 percent of the original capacity would result. Figure 9 shows the time it would take for a system to lose 25 percent of its original capacity depending upon system current density, storage duration, and reactant solution concentration.

Catalyst Level

Test results on several catalyst concentrations, with all other membrane characteristics constant, show a marked decrease in area resistivity with a decrease in catalyst concentration. Like other limitations mentioned above, there is also a limit to the degree of catalyst concentration reduction. Below a certain catalyst concentration polymerization does not take place, or takes place at an undesirably slow rate. The new standard membrane mentioned earlier has the lowest desirable catalyst concentration and the most desirable properties of experimental anion membranes as of this printing.

Crosslinker Density and Type

Test results on membranes which were made with varying crosslinker densities show resistivities that compare to each other closely. These values are not sufficiently low enough to be considered as candidates for improved formula variation. Selectivity values were also comparable to one another with the V + 10 samples having the lowest, most desirable selectivity value of $15 \mu\text{g Fe/hr/cm}^2$. Changes in the type of crosslinker included TMPTM (trimethylolpropanetrimethacrylate), 1,6-hexa (1,6-hexamethylenediol-dimethacrylate), and a blend of CDIL and CP4L (vinylbenzylchloride and 4-vinylpyridine).

Membrane Thickness

Studies on fabric backing thicknesses indicate that thinner fabric backing yields slightly lower area resistivity. Fabric backing thickness can be reduced further by a compression process called calendering. This improves resistivity slightly. Membrane thickness to date is nominally 15 mils.

The variations discussed above can be performed without changing the basic membrane chemistry or properties such as selectivity or resistivity. Other variations are presently being investigated that have resulted in changing the membrane formulation so that it would no longer be considered as CDIL chemistry.

Resistivities of all membrane variations generally increased as a function of time and iron concentration. Only the CDIL 20 NP and CDIL 25 NP showed no resistance increase in 0.5 M FeCl_3 /1 N HCl solution with other membrane formulations showing slight increases. At the 1 M FeCl_3 and 1.5 M FeCl_3 concentrations the fouling effect was much more noticeable. Resistivity of most membranes reached a constant value after about 40 hours, but some continued to increase during the testing period. Comparing the results in 1.5 M FeCl_3 solutions, the 2 N HCl level showed a much greater fouling effect than at the 1 N HCl level. This is apparently due to the greater formation of negative complexes at the higher acidity causing a larger degree of membrane charged sites fouling.

Recently developed membranes are not affected as much as the former standard CDIL. The past standard CDIL had a resistivity of $6.8 \Omega\text{-cm}^2$, while the new formulation gave a value of $5.4 \Omega\text{-cm}^2$ when equilibrated in 1.0 M FeCl_3 . For comparisons, results for the same membranes in 1.0 N HCl were $3.9 \Omega\text{-cm}^2$ for the past standard CDIL, and $3.6 \Omega\text{-cm}^2$ for the new formulation. The selectivities of the standard and the improved membranes are satisfactorily high at $15 \mu\text{g Fe/hr/cm}^2$ and $20 \mu\text{g Fe/hr/cm}^2$, respectively. The significant reduction in area resistivity with virtually no sacrifice in selectivity has increased the performance of operating Redox cells by reducing their overall internal resistance from 8 to $3.5 \Omega\text{-cm}^2$.

Formula Variations

Some studies with major variations in membrane chemistry were conducted. One of these variations (increasing functionality) involves the addition of functional sites to the membrane molecular structure. Crosslinkers and backbone monomers of differing length and numbers of functional sites are incorporated onto the membrane substrate. Since these changes greatly affect membrane properties and structures they are no longer classified as

CDIL chemistry. In table II, increased functionality membranes are compared to the new standard CDIL. On the whole, these membranes have significantly lower area resistivities than past membranes. However, the selectivity of these samples was too low for applications in the Redox storage system. Research in this area will continue in an attempt to increase selectivity without losing the good resistivity.

Cell Performance

In figure 10 the polarization performance of the past standard CDIL and the improved formulation in a 14.5 cm² Redox cell are compared. A cell voltage of 0.9 volt was chosen as a common reference point for comparison with other cells. The interim goal for cell output is 50 amperes per square foot at 0.9 volt at 50 percent depth of discharge. This corresponds to a membrane area resistivity of about 3.0 Ω -cm² after equilibrium within a Redox cell.

Figure 11 shows the performance of the improved formulation, which is now the present standard or new standard membrane, in 1.0 M Fe/Cr and 1.5 M Fe/Cr solutions. The slope of these polarization curves indicates that the membrane resistance increases in higher concentrations of Fe⁺³. This agrees with membrane fouling data discussed earlier in this paper. Notice that the 1.5 M Fe/Cr curve with the new standard membrane is similar to the performance of the past standard membrane with 1.0 Molar solutions.

SUMMARY OF RESULTS

Present findings indicate that NP level should be fixed between 25 and 27.5 in order to yield membranes which are more selective and possess lower area resistivity. 30 and 40 NP Membranes were found to be too open for separation of the Redox reactants. Smaller NP numbers than 25 yield membranes with undesirably high area resistivity.

The proper concentration of catalyst appears to be an important factor in lowering area resistivity. It was found that lowering catalyst concentration to 0.0625 decreased area resistivity by about 50 percent. Catalyst levels below 0.0625 do not allow proper curing and membranes will not solidify properly, but remain in the gel state.

Membrane thickness is controlled by fabric backing thickness, which can be squeezed slightly to make the final product approximately 50 percent thinner. This process reduces resistivity slightly. Membranes are presently 15 mil thick nominally.

Studies conducted thus far indicate that resistivity is affected by a change in crosslink density and type of crosslinker. Increasing crosslink density appears to increase area resistivity slightly. Substitution of one crosslinking agent for another has a more profound effect on resistivity because of the more complex chemistry involved. So far, a crosslinker which produces membranes with an area resistivity lower than the present standard has not been found.

New membranes are now being developed and tested which have incorporated additional chemical functional sites on the polymer chain. Increasing the functionality sites in this manner has resulted in membranes which have lower area resistivity than the present standard. At this point in time, however, the selectivities of these new formulations are too low to be acceptable in a Redox application.

The best membrane currently developed for use in the NASA-Redox Energy Storage System is the COIL-AA5-0.0625 catalyst anion exchange membrane made by Ionics, Inc. of Watertown, Massachusetts. The characteristics of this membrane type are as follows: Thickness = 0.035 - 0.040 cm, Water content = 39 - 42 percent, Selectivity = 20 $\mu\text{g Fe/hr/cm}^2/\text{M/L}$, Resistivity ($\Omega\text{-cm}^2$) = 3.6 in 1 N HCl, 3.9 in 0.5 M Fe^{+3} , 5.4 in 1.0 M Fe^{+3} , and 10.3 in 1.5 M Fe^{+3} . (All iron solutions used in resistivity tests were diluted with 1.0 N HCl.) This membrane has a low resistivity and acceptable selectivity. There is a slight Fe^{+3} fouling effect as is observed in the resistivity figures, and consequently, better resistance stability.

CONCLUDING REMARKS

Anion exchange membranes for the NASA-Redox Energy Storage System have been developed to the point of almost meeting selectivity and resistivity standards for solar-photovoltaic stand-alone systems and applications. This reflects a significant improvement in understanding the membrane properties and the techniques for controlling those properties. More research is in progress to develop membranes for Redox systems for use in electric utility applications which require more stringent controls of selectivity and resistance stability.

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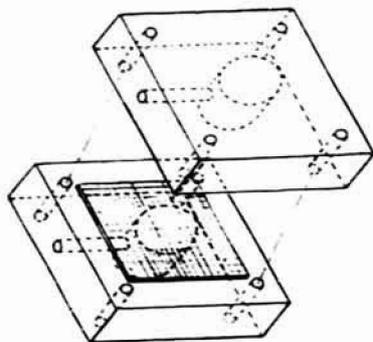
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TABLE I. - RESULTS OF SELECTIVITY AND RESISTIVITY FLOW TESTS OF
MINOR FORMULATION VARIATIONS
[1 M FeCl₃ and 0.5 N HCl used in ferric selectivity tests]

Variation	Area resistivity - Ωcm^2								Selectivity $\mu\text{g Fe/hr/cm}^2$ (Ferric ion)
	1 N HCl	2 N HCl	0.5 M Fe 1 N HCl	0.5 M Fe 2 N HCl	1 M Fe 1 N HCl	1 M Fe 2 N HCl	1.5 M Fe 1 N HCl	1.5 M Fe 2 N HCl	
NP and catalyst variations									
Past standard									
CDIL - 25 NP (0.5 CAT)	3.9	---	3.9	---	6.8	---	21.8	---	15
CDIL - 20 NP (0.5 CAT)	4.8	---	4.8	---	8.6	---	34.8	---	7
CDIL - 25 NP (0.0625 CAT)	3.5	2.3	3.9	2.6	5.2	5.4	10.3	19.7	20
New standard									
CDIL - 27.5 NP (0.0625 CAT)	3.6	2.0	3.9	2.8	5.4	5.4	10.3	18.4	21
CDIL - 27.5 NP (0.25 CAT)	3.5	2.8	---	3.0	---	6.2	---	20.0	16
Variation of crosslinker type									
1,6 Hexa - 50%/VBC - 50%	3.8	2.2	4.2	3.0	6.1	5.7	12.2	22.0	27
1,6 Hexa - 25%/VBC - 75%	4.1	2.3	4.5	3.0	6.8	5.9	12.4	23.2	25
1,6 Hexa - 100%	3.9	2.2	4.1	3.0	6.5	6.1	13.2	27.1	30
TMPTMA/DMAEMA	6.4	3.8	6.7	4.8	8.6	7.5	13.5	17.0	17
CDIL - 50%/CPAL - 50%	3.6	3.0	---	3.9	---	10.6	---	44.5	12
Variation of crosslinker density									
V + 10 - 25 NP	3.6	2.8	---	3.0	---	6.5	---	22.5	16
D + 20 - 25 NP	3.3	2.8	---	2.8	---	5.8	---	16.7	30

TABLE II. - PROPERTIES OF MEMBRANES WITH INCREASED FUNCTIONALITY
COMPARED TO NEW STANDARD

Membrane	Resistivity, - Ωcm^2				Selectivity, $\mu\text{g Fe}^{+3}/\text{hr/cm}^2/\text{M/L}$
	1 N HCl	0.5 M Fe ⁺³	1.0 M Fe ⁺³	1.5 M Fe ⁺³	
Long difunctional	2.18	---	3.19	4.35	179
Short difunctional	2.76	---	3.77	4.93	75
Trifunctional	2.76	---	3.77	4.93	81
50 Percent tetrafunctional/ 50 Percent difunctional	2.47	2.62	3.77	6.96	81
100 Percent tetrafunctional	2.76	2.90	4.64	8.12	66
Di/tri/tetrafunctional (mixture)	2.76	3.92	5.80	14.94	37
New standard	3.48	3.92	5.22	10.30	20



MEMBRANE IS PLACED AS SHOWN AND HALF CELLS ARE BOLTED TOGETHER

Figure 2 - Static diffusion/selectivity apparatus.

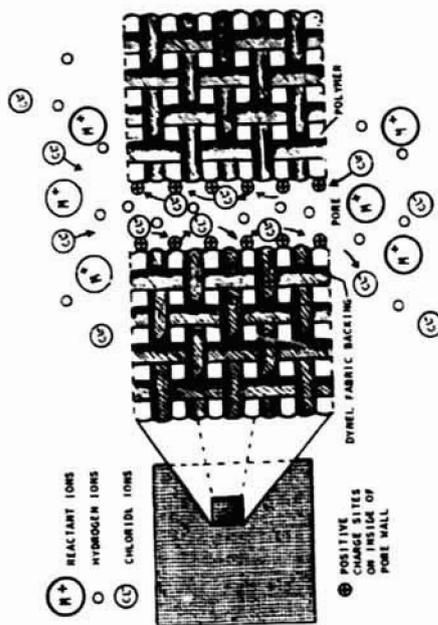


Figure 1 - Magnified section of basic membrane structure.

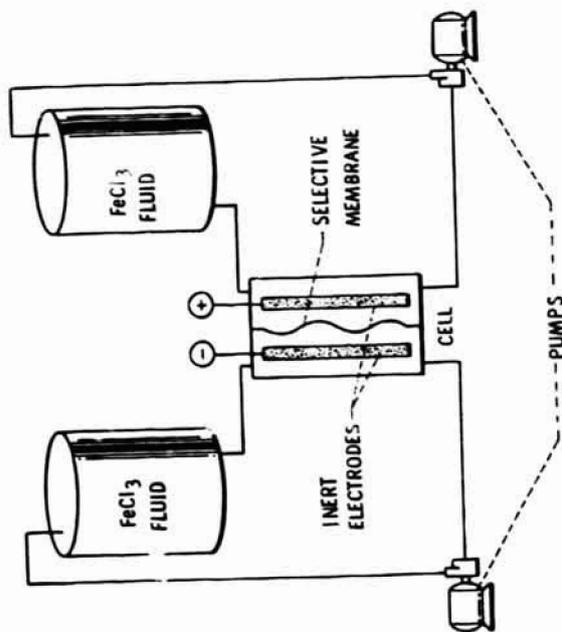


Figure 3 - Iron/iron resistivity flow cell.

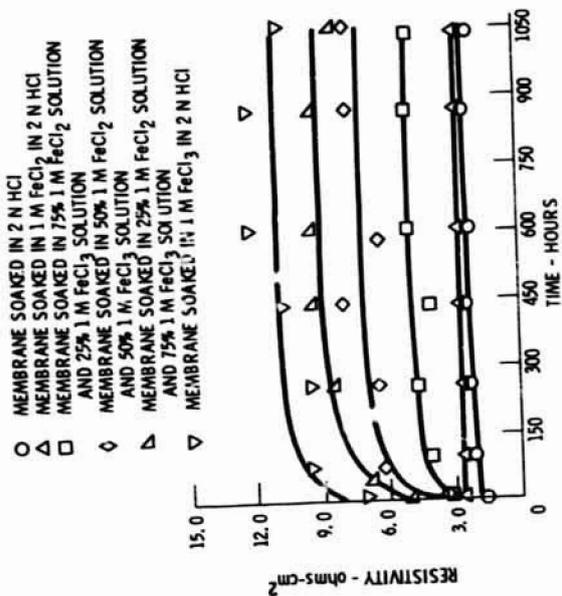


Figure 4 - Effect of iron chloride soaks on CDIL-A5-25NP area resistivity.

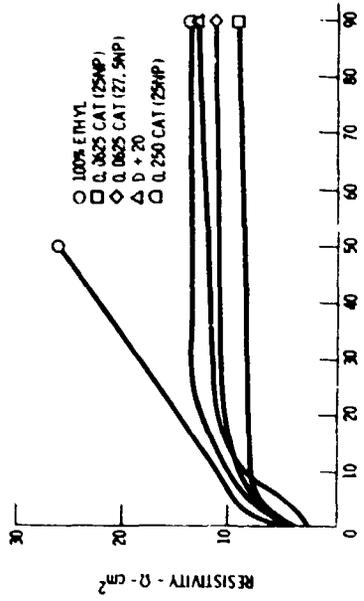


Figure 6. - Resistivities of CDL formulations in an Fe^{+3} flow cell.

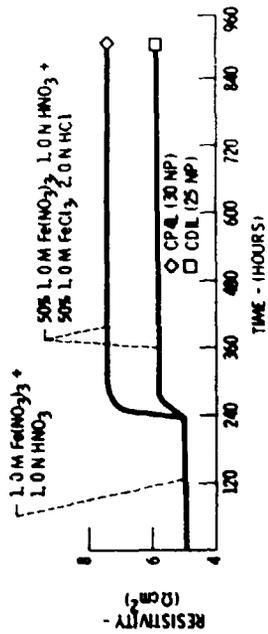


Figure 5. - Effect of iron nitrate soaks on membrane area resistivity.

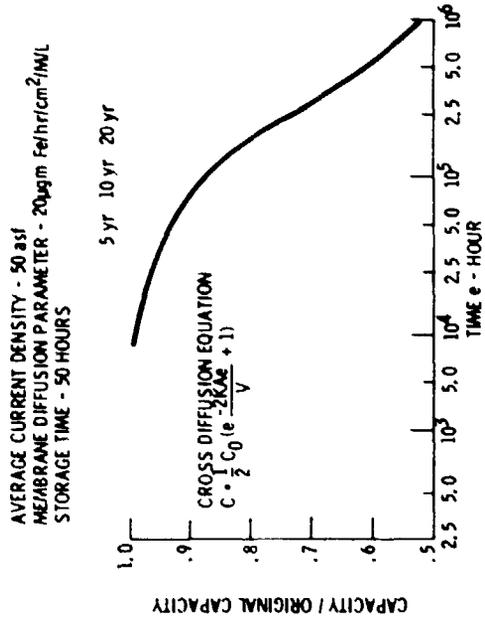


Figure 8. - Capacity retention estimate for redox system.

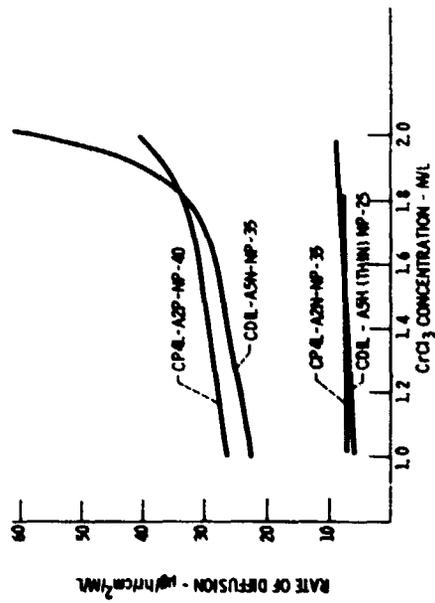


Figure 7. - Cr^{+3} transfer in anion membranes as a function of $CrCl_3$ concentration.

BASIS: MEMBRANE CROSS DIFFUSION RATE - 10.0 $\mu\text{GMHR}/\text{CM}^2/\text{MIL}$

CURRENT DENSITY ASF	STORAGE DURATION HOURS	CROSS DIFFUSION RATE MOLES/LITER	CONCENTRATION	TIME YEARS
25	50	1	1	22
50	10	1	1	8.6
100	5	1	1	8.6
50	10	2	2	4.3

NOTE:

- 1 - HALVING THE CROSS DIFFUSION RATE WOULD DOUBLE ALL TIMES
- 2 - DOUBLING THE CURRENT DENSITY WOULD DOUBLE ALL TIMES
- 3 - HALVING THE STORAGE DURATION WOULD CUT THE TIMES IN HALF

Figure 9. - Calculated time for 25% loss of original capacity.

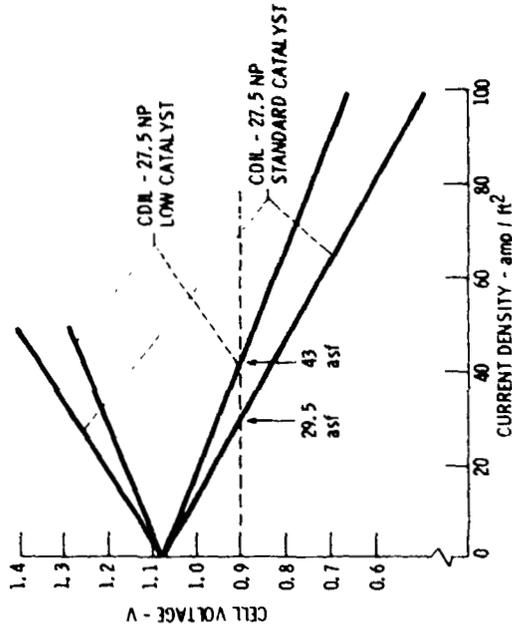


Figure 10. - Improved cell performance with newly developed membrane.

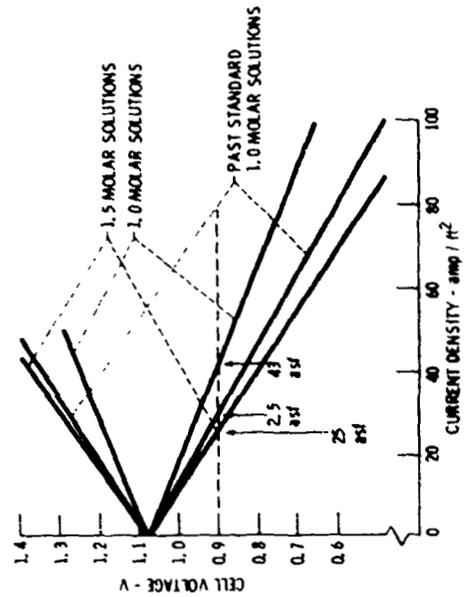


Figure 11. - Comparison of recent cells using 1.0 molar solutions with cells using 1.5 molar solutions.