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# **NASA Redox Storage System Development Project**

**Calendar Year 1981**

National Aeronautics and Space Administration  
Lewis Research Center

**April 1983**

Prepared for  
**U.S. DEPARTMENT OF ENERGY  
Conservation and Renewable Energy  
Division of Energy Storage Systems**

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**Calendar Year 1981**

National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

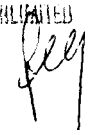
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# CONTENTS

	Page
Summary . . . . .	1
Chromium Reactant Electrochemistry . . . . .	3
Single-Cell Studies . . . . .	6
Thermal Effects . . . . .	9
Totally heated system . . . . .	9
Heated, then quenched, reactant . . . . .	10
Life (Endurance) Tests . . . . .	13
Iron-Hydrogen Rebalance Cell . . . . .	15
Premixed Reactants . . . . .	15
Four-Tank Operation . . . . .	17
Electrode Development . . . . .	19
Carbon Felt Processing Temperature . . . . .	19
Chromium Electrode Reproducibility . . . . .	20
Planar Electrodes . . . . .	22
Giner, Inc. . . . .	25
Membrane Development . . . . .	26
Ionics, Inc. . . . .	27
NASA Lewis Research Center . . . . .	33
Reactant Costs . . . . .	35
Concluding Remarks . . . . .	39
References . . . . .	40
Bibliography . . . . .	41

## SUMMARY

During 1981, much was accomplished in developing an understanding of the behavior of the chromium ion species during the operation of an iron-chromium Redox cell. Puzzling performance characteristics such as poor charge acceptance rates, unavailable capacity, and a hysteresis effect on cell open-circuit voltage, depending on whether charge or discharge is taking place, were explained. The governing factors were shown to be the relative concentrations of chromium ion species and the rates of equilibrium between the species. Even more importantly, it was shown that by heating the chromium solution to 120° to 150°F (49° to 66° C), the equilibria between species can be speeded up and shifted to favor the more electrochemically active species. This greatly alleviates the performance characteristics noted above. Furthermore the need to go to higher temperatures, dictated by the preceding considerations, has additional benefits. It greatly simplifies and reduces the cost of heat rejection from complete systems and, as discussed in the following section, reduces cell resistance and thus further improves energy efficiency.

The necessity for operation at higher temperatures is having and will continue to have a profound effect on test procedures and component development tasks. Properties of membranes and electrodes must be reevaluated at the higher temperatures; formulations and preparations of these components may require modification in order to satisfy performance targets under the new operating conditions. System-level considerations, such as conceptual design and operating procedures, should be rethought in terms of thermal management, startup, etc.

Iron and chromium reactants can become chemically out of balance in several ways. One is by the intrusion of air (oxygen) into either of the reactant systems; the other is through the evolution of hydrogen, which occurs to a greater or lesser degree from the chromium electrode. In either case the net result is that the iron reactant solution is at a higher state of charge than the chromium. This manifests itself as a loss of capacity. This condition is easily corrected at the system level by using an electrochemical cell to combine the excess charged iron with hydrogen. Hydrogen is supplied either externally or from the chromium system, if it is being generated. A modification to the original rebalance cell design has resulted in improved performance (lower polarization), better reproducibility of performance, and much less required maintenance.

Operation of a Redox system with totally premixed reactants would offer, in principle at least, several advantages over the standard approach of using a highly selective membrane to keep the reactant solutions separate. Microporous separators could be used, making cell resistance much lower and also greatly reducing cell cost. Any tendency toward fluid transfer could be countered simply by pumping fluid back to the diminished reservoir. Use of more highly concentrated reactant solutions would result in lower tankage cost. Also, it would not be necessary to start with excess reactant quantities to compensate for reactant crossmixing during the life of the system. The disadvantages of the mixed-solution approach would be a decrease in coulombic efficiency, due to reactant mixing and self-discharge across the microporous separator, and an increase in reactant costs. However, the reactant cost studies discussed later indicate that these costs may still be acceptable. Some preliminary experimental work was done in 1981 to examine concept feasibility and some of the various trade-offs.

In the present two-tank iron-chromium Redox system configuration, there is for each reactant a continuous mixing of solutions at different states of charge as the reactant circulates continuously between its tank and the cells. This results in changes in the effective reactant activities such that there is a reduction of system efficiency. Some of this loss can be avoided by using two tanks for each solution, one acting as a receiver for the partially spent reactant leaving the cell (or cells). Discharge and charge would then proceed in constant-voltage steps. This concept has been successfully evaluated in the laboratory and indicates that the four-tank concept could improve system round-trip energy efficiency by 3 to 5 percentage points.

The primary focus of the electrode development task during 1981 was to make possible and to verify the reproducible fabrication of satisfactory chromium Redox electrodes. Carbon felt or graphite felt substrates, processed at six temperatures and then catalyzed to form electrodes, were evaluated in terms of chromium reduction activity and hydrogen evolution rate. An optimum processing temperature range was determined to yield felts that, when cleaned and catalyzed, produced electrodes with adequate chromium reduction rates and acceptably low hydrogen evolution. Reproducibility of performance was established by identically preparing and testing a series of chromium electrodes in complete Redox cells. A second-level effort was to prepare and evaluate several cells in which the usual carbon/graphite felt electrodes were eliminated, leaving only the planar carbon collector plate surfaces to serve as the active electrodes. The planar electrode studies show that these surfaces, while active, apparently have a linear component of kinetic polarization that causes performance to be lower than that of the standard felt electrodes.

The primary goal of the membrane development program during the year was to evaluate variations in the resin formulation and the substrate of the standard CD1L-AA5-LC membrane. Improvements were sought in membrane resistivity, selectivity, and cost. Reduction of resistivity was attempted through the use of substrates thinner than the standard calendered, woven modacrylic. Woven and nonwoven polyethylene, polypropylene, and polyester were evaluated, as were various laminate constructions. Reduction of membrane cost was attempted through the replacement of the standard vinylbenzyl chloride (VBC) component with the less expensive dichloroethylene (DCX). Another variation in the standard resin formulation, intended to increase selectivity by increasing the ion exchange capacity of the resin, was to reverse the relative quantities of VBC and the dimethylaminoethyl methacrylate (DMAEMA) components. Although some of these variations resulted in membranes that were equivalent to or marginally better than the CD1L standard, none offered the significant improvements being sought. The net result of the year's development effort was to show that the standard CD1L membrane still offers the best combination of desirable properties. These properties must now be reevaluated at the higher temperatures that have been shown to be desirable.

Two contract efforts are under way to determine the cost of producing the iron and chromium redox reactants (ferrous chloride and chromic chloride) in large quantities, sufficient to provide one-hundred new 100-MWh Redox storage systems annually. The studies are being carried out by Allied Chemical Corp., a large producer of chromium chemicals, and Charles River Associates, a consulting firm with a strong background in hydrometallurgical processes. A wide spectrum of possible production methods are being evaluated. The preliminary results of these studies are extremely encouraging, projecting costs as low as 40 percent of previous cost estimates that had been assumed to be quite optimistic.



In summary, then, the main result of the year's program was the achieving of a deeper understanding of the basic characteristics of the iron-chromium Redox system. Modifications to the basic system concept are showing themselves to be attractive from both cost and efficiency standpoints. Also, concern that the use of chromium chemicals is too costly is being seriously challenged.

### CHROMIUM REACTANT ELECTROCHEMISTRY

It has long been known that for complex ions of chromium (III), unlike those of almost all other transition metal elements, the rate of substitution of one ligand (complexing species) for another is extremely slow. Very early in the work with the iron-chromium Redox system, it became apparent that this characteristic played a major role in the electrochemical behavior of the Cr(II)/Cr(III) couple. An anomaly in the chromium electrode behavior manifested itself at room temperature, during a charge-discharge cycle, in the sequence of chromium solution color changes shown in figure 1, in a hysteresis in the open-circuit-versus-state-of-charge curve (fig. 2), in poor charge acceptance rates during a constant-voltage charge (fig. 3), and in cell voltage changes during a constant-current charge (fig. 4).

The color sequence during a cycle (fig. 1) progressed from a dark blue-green at full discharge to blue at about 60-percent state of charge (SOC). The blue then persisted, becoming lighter during the remainder of the charge. However, after about 10-percent discharge the blue-green color returned.

It is known that a chromic chloride solution could contain the blue-green  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$  and the blue  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  ions. Thus it was postulated that the solutions being used initially contained a mixture of the pentahydrate and the hexahydrate and that during charge the pentahydrate was reduced first, leaving the blue hexahydrate, which was reduced with much greater difficulty. The slowness of reestablishing equilibrium between the species (the characteristic of chromium (III) ligands noted above) is the cause of the near-total depletion of the pentahydrate species.

On the other hand, the chromium (II) species, unlike the chromium (III) species are labile (i.e., equilibrium between the complex species is rapidly attained). Therefore oxidation of the chromous species directly to the chromic pentahydrate during discharge would explain the production of a blue-green color after only a small amount of discharge.

The same sort of rationale can be used to describe the open-circuit-voltage-versus-state-of-charge curve (fig. 2). If a given SOC is attained by charging from a lower SOC, instead of by discharging from a greater SOC, the chromium solution will have a greater amount of the less-reactive hexahydrate species. Being the more stable species, the hexahydrate would have a greater negative free energy of formation and would therefore be expected to evidence a greater open-circuit voltage.

As of early 1981, no electrochemical measurements had been made of the behavior of the various chromium (III) species on the gold-lead chromium electrode catalyst developed by NASA Lewis and Giner, Inc. However, the literature for mercury electrodes (refs. 1 and 2) indicates that the blue-green pentahydrate is much more readily reduced than the blue hexahydrate. Subsequent voltammetry, comparing the activities of pure hexahydrate solutions and solutions of mixed hexa- and pentahydrate on the gold-lead catalyst, revealed a similar, greater electrochemical activity when the pentahydrate was present. These same considerations concerning the depletion of the more active pentahydrate species during charge explain the sudden drop in charge acceptance at about 40-percent SOC during a constant-voltage charge at room temperature (fig. 3) and the rapid rise in voltage during a constant-current charge (fig. 4).

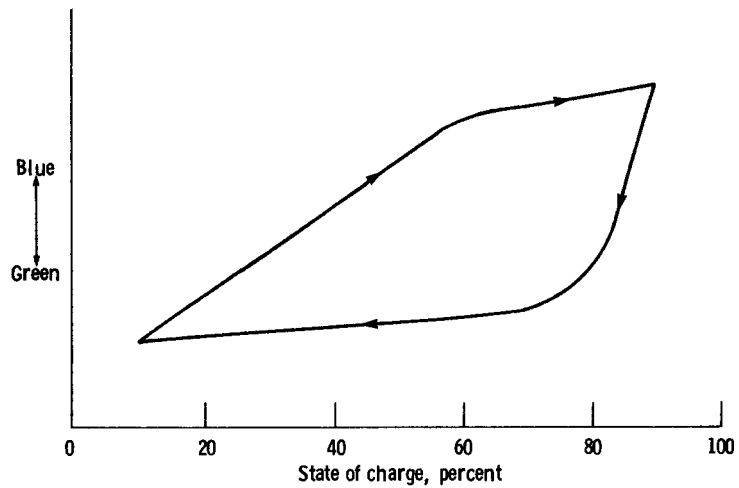


Figure 1. - Chromium solution color changes during a charge-discharge cycle at room temperature, showing hysteresis.

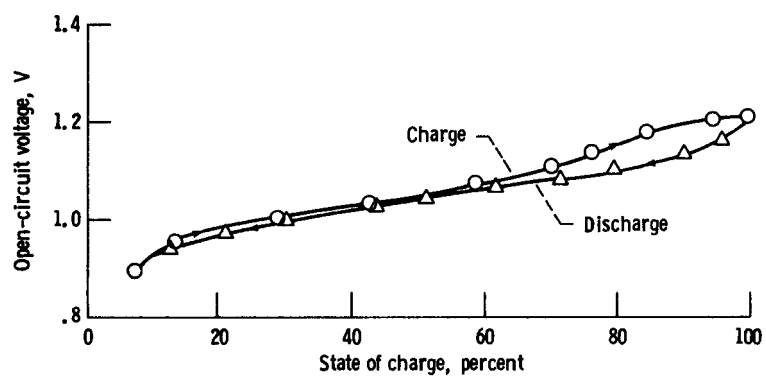


Figure 2. - Cell open-circuit voltage during a charge-discharge cycle at room temperature, showing hysteresis. Current density, 21.5 mA/cm<sup>2</sup>.

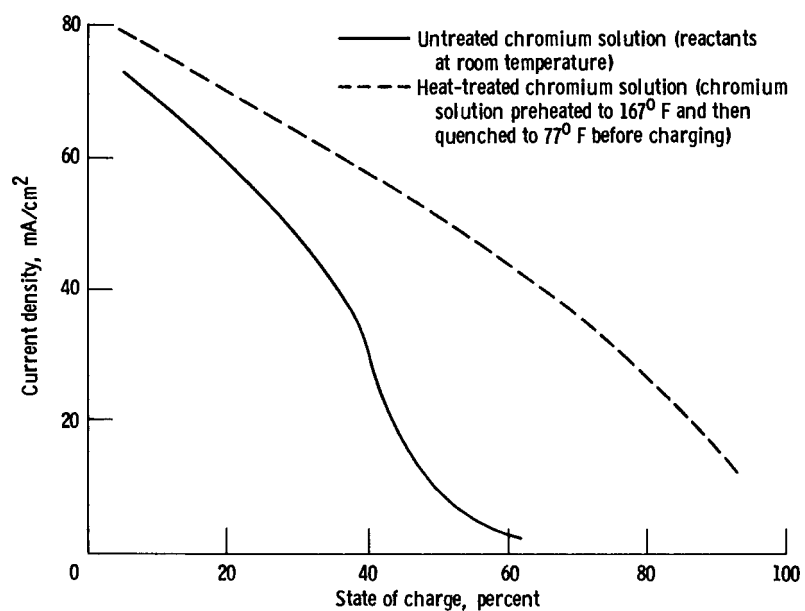


Figure 3. - Constant-voltage charge acceptance of an iron-chromium Redox cell. Charging voltage, 1.3 V; cell area, 14.5 cm<sup>2</sup>; single cell.

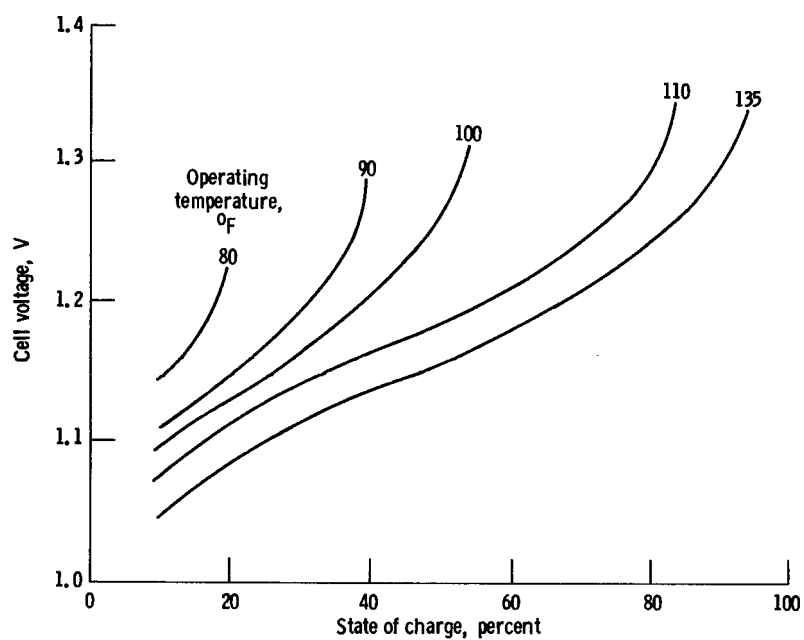


Figure 4. - Constant-current charge performance of iron-chromium Redox cell as a function of operating temperature. Current density, 32.3 mA/cm<sup>2</sup>; cell area, 14.5 cm<sup>2</sup>; single cell.

During the past 2 years a faculty member of Spring Arbor College, both as a Summer Faculty Fellow at Lewis and as recipient of a grant from Lewis, working with Lewis personnel, confirmed and quantified these hypotheses by using spectrophotometry and ion-exchange separation techniques (ref. 3). Measurements of the chromium half-cell potential during the charging of a cell, in conjunction with simultaneous spectrophotometric determinations of the various chromium species present, were used in figure 5 to further reinforce the conclusion that the pentahydrate is the active chromic species. In this figure the logarithm of the reactant-to-product concentration ratio, with the "product" defined in three ways, is plotted against the half-cell open-circuit potential. Only when the pentahydrate species alone was treated as the product did a straight line, with a slope of 64 mV/decade, result. This closely satisfies the Nernstian criterion of a straight line with a slope of 59 mV/decade.

Another presentation of the spectrophotometric data is given in figure 6, where the concentrations of the chromic hexa- and pentahydrate complexes measured periodically during a charge-discharge cycle are shown. Here again, the pentahydrate is shown to be the active species.

The result of all of these observations and investigations was the conclusion that some means had to be uncovered to permit the charging of an iron-chromium Redox cell, at an acceptable rate, to a high state of charge, without applying excessive voltage. This seemed to indicate the need of an electrocatalyst that would promote the direct reduction of the chromic hexahydrate complex at the chromium electrode or a catalyst that would enhance the equilibrium kinetics between the hexa- and pentahydrate species. To date, the search for such catalysts has been unsuccessful.

However, during 1981 it was determined that raising the temperature of the chromium solution increased the rate of equilibration between the chromic species and shifted the equilibrium to favor the desired pentahydrate complex (fig. 7). It was also ascertained that the higher pentahydrate concentration at a high temperature could be "frozen in" by rapidly cooling, or "quenching," the heated solution back to room temperature. This was the approach taken for the first in-cell tests of pentahydrate-rich solutions. The results, discussed in greater detail in later sections, verified that much higher charging rates, out to 90-percent SOC, could indeed be sustained.

From the standpoint of complete storage system operation, it has long been known that, for any reasonably sized system, waste-heat rejection requirements would require operation at temperatures greater than the warmest expected ambient conditions. This situation, along with the beneficial effect of high temperatures on chromium solution chemistry as previously discussed, gave impetus, especially during the latter portion of the year, to a refocusing of the Redox project effort toward a consideration of higher-temperature operation.

Of course, high temperature not only increases the rate of heat rejection and shifts the equilibrium of the complexes to the more desirable pentahydrate species, but also has many other effects. These include effects on membrane resistivity, rates of crossmixing, possible membrane degradation, hydrogen evolution rates, and conductivity and viscosity of the solutions. These effects are now being investigated in order to ascertain the optimum operating temperature and Redox system configuration.

#### SINGLE-CELL STUDIES

As discussed in succeeding sections, out-of-cell screening techniques can be applied to specific cell components such as electrodes and membranes.

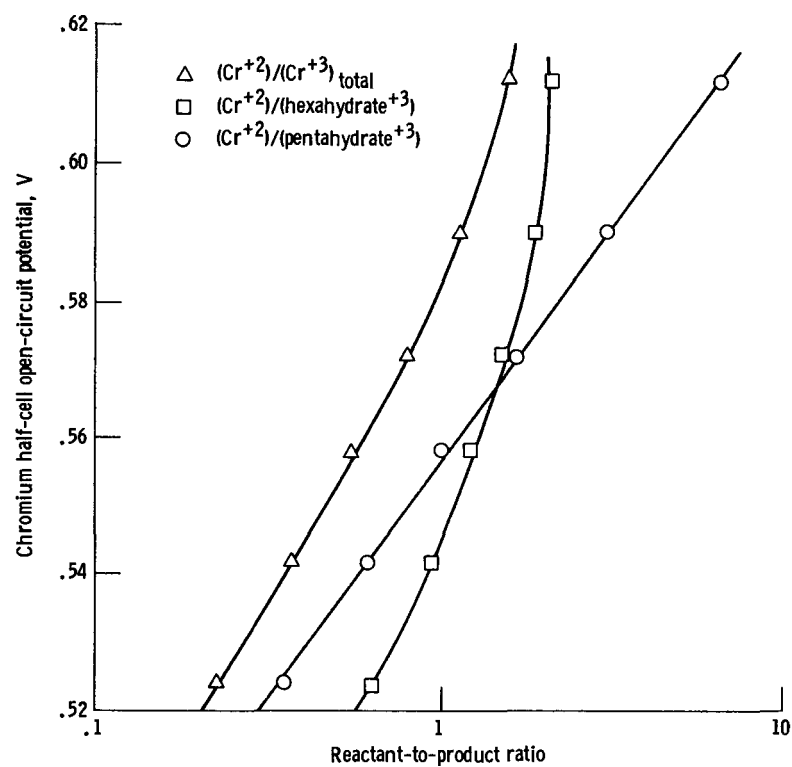


Figure 5. - Chromium half-cell open-circuit potential during charge as a function of logarithm of reactant-to-product ratio for three definitions of product - a Nernst equation correlation. Reference: Ag/AgCl.

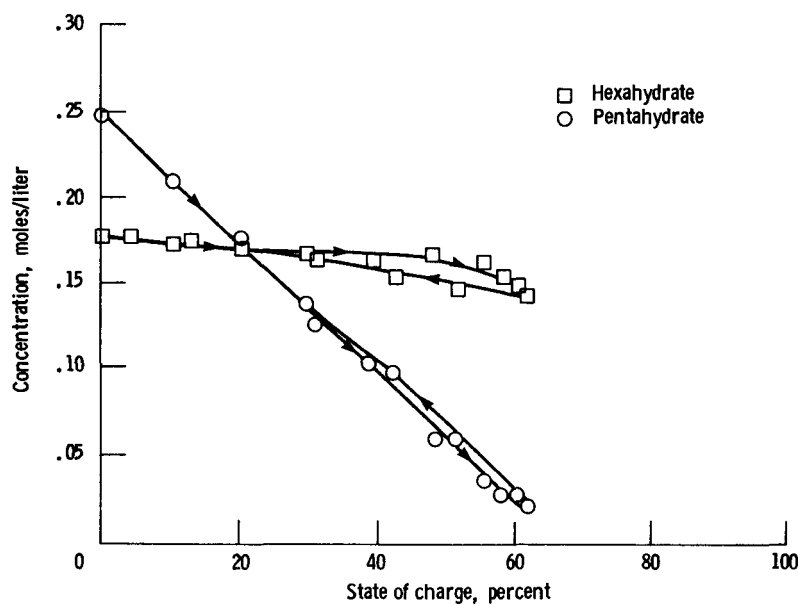


Figure 6. - Changes in concentration of two chromic ion complexes during charge-discharge cycle.

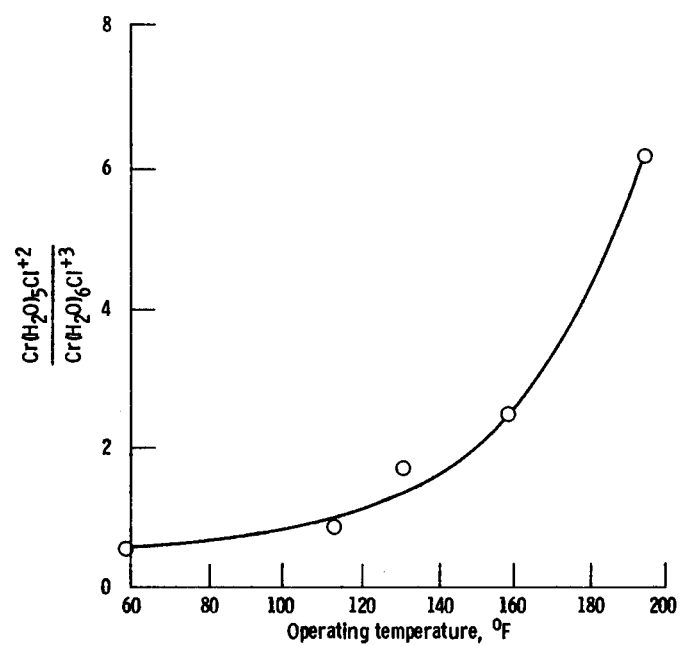


Figure 7. - Equilibrium between two chromic ion complexes as a function of operating temperature.

However, the quality and usefulness of such components must be verified in an operating iron-chromium Redox cell. In-cell tests are also required for the evaluation of varied operating conditions and environments, alternative configurations or concepts of operation, and unique functional capabilities. During 1981 single-cell studies were carried out for all of these reasons; these studies are discussed in this section.

Single-cell testing typically consisted of performing continuous charge-discharge cycles with cells of 14.5-cm<sup>2</sup>, 320-cm<sup>2</sup>, or 930-cm<sup>2</sup> active area on automated test stands. Periodically charge and discharge polarization curves were obtained at one or more states of charge. Cell and component characteristics measured during such testing, or inferred from the test results, included membrane resistance and resistance stability, polarizations, round-trip coulombic efficiency, electrode reversibility, electrochemical activity for charge and discharge, catalyst stability, and hydrogen evolution rates.

### Thermal Effects

In the past, basic experiments and single-cell testing have been conducted at the laboratory ambient temperature. However, as discussed in the previous section, there are significant advantages to operation of the iron-chromium Redox system at higher temperatures. Primarily these are the greater ease of rejection of waste heat, the reduction of cell resistivity with temperature, and the improved charge acceptance rates resulting from the thermal shift of the chromic ions to the electrochemically active pentahydrate form. These last two thermal characteristics are being evaluated in single cells in two modes: totally heated, where the entire test system is maintained at high temperatures; and quenched, where the uncharged chromium solution is heated and then cooled back to room temperature before entering the single cell for charging.

Totally heated system. - Experiments were conducted to determine the effect of temperature on overall cell performance as well as on cell resistance, open-circuit voltage, and hydrogen evolution rate. It is generally known that the resistance of a cell increases as the state of charge is increased and varies inversely with fluid temperature. The interaction of these trends requires investigation in order to determine optimized operating regimes for total systems. Needless to say, investigation is also necessary to establish proper thermal management as well as to set limits on system operating conditions and component design. To bring all system elements to the given test temperature, the conventional test system, consisting of a single 14.5-cm<sup>2</sup> working cell and a rebalance cell (discussed in a later section), was packaged for placement in an insulated enclosure. Only the pumps were located outside the enclosure, as their motors could be damaged by prolonged high-temperature operation and since they would not ordinarily be subjected to the high temperatures of the main system components anyway. A Pyrex glass heat exchanger coil was immersed in a glycol heating medium to bring each solution to the designated operating temperature. The rest of the system (less pumps) was floated in a tray above the glycol bath and subjected to the ambient heated air in the enclosure hood. The temperature range 80° to 150° F was empirically established as the range of interest for testing.

Polarization measurements were made on the isothermal system at 25-, 50-, and 75-percent states of charge over the range 80° to 150° F, in 10 deg F increments. The performance with standard solutions of 1.0 M chromium and

iron, respectively, in 2.0 N HCl was compared with that with isotonic solutions consisting of 0.9 M Cr and 1.1 M Fe in 1.0 N HCl or in 0.5 N HCl. The runs, conducted at 50-percent SOC are shown in figure 8 for selected temperatures, generally in the 80° to 150° F range. The curves reveal that the best performance, indicated by the charge-discharge plots with the minimum slope, was in the range 110° to 120° F for the 1.0 M reactants prepared in 2.0 N HCl and 140° to 150° F for the isotonic solutions prepared in 1.0 N HCl or in 0.5 N HCl. These observations agree with the fact that greater HCl concentrations and higher temperatures both promote the formation of the anionic chloro complexes of the ferric ion, which in turn foul the membrane and increase resistivity. Therefore the greater the HCl concentration, the lower the temperature at which fouling becomes significant.

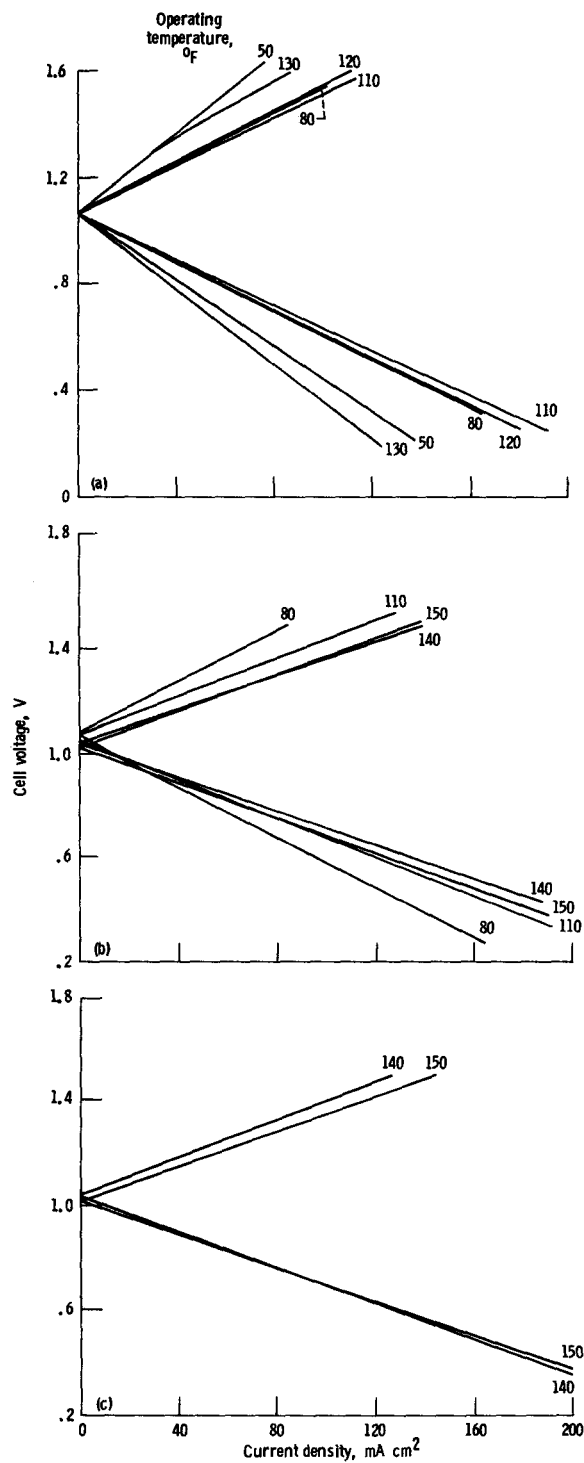
Temperature sweeps were made in 5 deg F steps over the range 80° to 150° F, at constant states of charge, and the corresponding cell resistances were recorded. The results are shown in figure 9. Here, the SOC had a larger effect for reactant solutions acidified to 2.0 N HCl than for the less acidic isotonic solutions, with the least influence of SOC shown for 0.5 N HCl isotonic reactants. At low SOC, where the complexing of the ferric ion is not very significant, reducing the HCl concentration reduced solution-membrane conductivity and raised the cell resistance. At high SOC, reducing the HCl concentration reduced the complexing of the ferric ion, with its attendant membrane fouling and thus lowered the cell resistance. For the 2.0 N HCl solutions the minimum resistance occurred in the range 110° to 125° F. The best operating range for the polarization tests (fig. 8(a)) verified this. Similarly, the best operating range for 1.0 N HCl isotonic solutions was 130° to 150° F, with a slight shift to even higher temperatures for the 0.5 N HCl isotonic solutions.

The effect of increasing temperature on constant-current charge acceptance is shown in figure 10. The change in performance with temperature indicates the significant equilibrium shift of the chromium species to the more reactive pentahydrate species. The rapid voltage rise occurs as the chromium solution is depleted of the pentahydrate and only the unreactive hexahydrate remains.

Heated, then quenched, reactant. - Since the chemical equilibrium between the complex species of the chromic ion in the chromium solution can be shifted rapidly at higher temperatures to favor the electrochemically active pentahydrate form, a 14.5-cm<sup>2</sup> single-cell system was constructed to heat the chromium solution and then quench it back to room temperature while keeping the remainder of the system at room temperature. This approach, which takes advantage of the fact that the equilibrium shift back toward the hexahydrate at room temperature is slow, focuses on performance changes resulting from the increase in the pentahydrate species concentration and eliminates thermal effects on membrane and electrode properties. Voltage-current relationships and hydrogen evolution as a function of SOC were recorded.

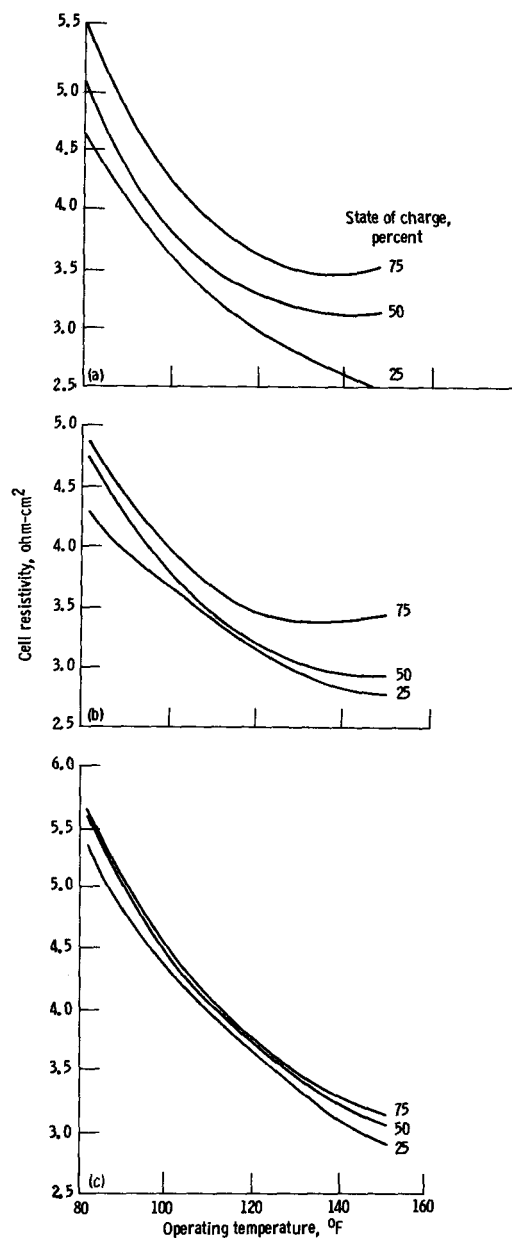
The influence of the history of the chromium solution on the cell constant-current charging characteristic is shown in figure 11. The reactivity of a chromium solution that had aged at room temperature is compared with that of a solution that had been recently heated and quenched. The solution aged 2 weeks at room temperature (cycle 1) had poor charging performance because of the rapid depletion of the active pentahydrate species. The chromium solution equilibrated at 167° F for about 0.5 min, quenched, and then immediately charged (cycle 2) had much better charging performance. Allowing equilibration for 1 more day at room temperature shifted performance back toward that of the 2-week-equilibrated solution (cycle 3). Also shown in figure 11 is the idealized Nernstian performance for the same cell.





(a) 1.0 Molar iron and chromium; 2.0 N HCl.  
 (b) 0.9 Molar chromium; 1.1 molar iron; 1.0 N HCl.  
 (c) 0.9 Molar chromium; 1.1 molar iron; 0.5 N HCl.

Figure 8. - Polarization performance at 50-percent state of charge as a function of operating temperature. Cell area, 14.5 cm<sup>2</sup>; single cell; membrane, CD1L-AA5-LC.



(a) 1.0 Molar iron and chromium; 2.0 N HCl.  
 (b) 0.9 Molar chromium; 1.1 molar iron; 1.0 N HCl.  
 (c) 0.9 Molar chromium; 1.1 molar iron; 0.5 N HCl.

Figure 9. - Cell resistivity as a function of operating temperature and state of charge.

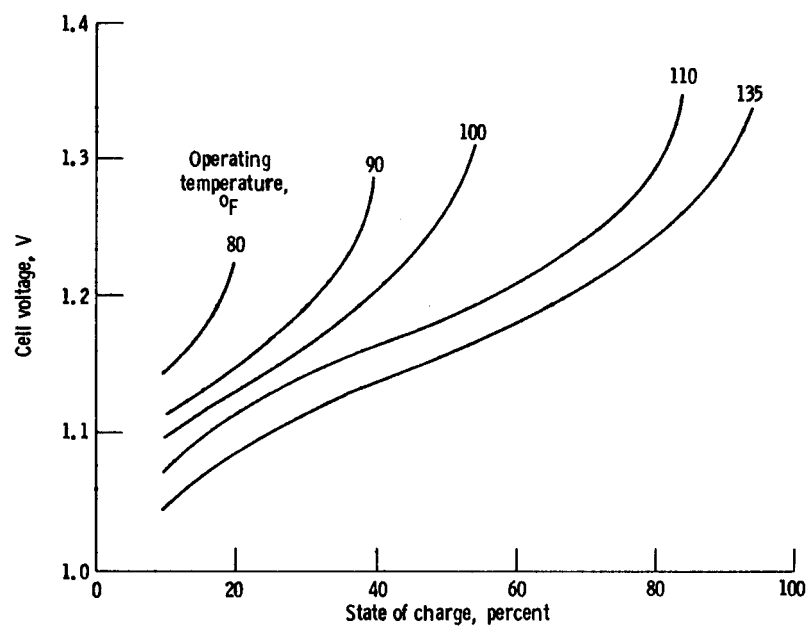


Figure 10. - Constant-current charge performance of iron-chromium Redox cell as function of operating temperature. Current density, 32.3 mA/cm<sup>2</sup>; cell area, 14.5 cm<sup>2</sup>; single cell.

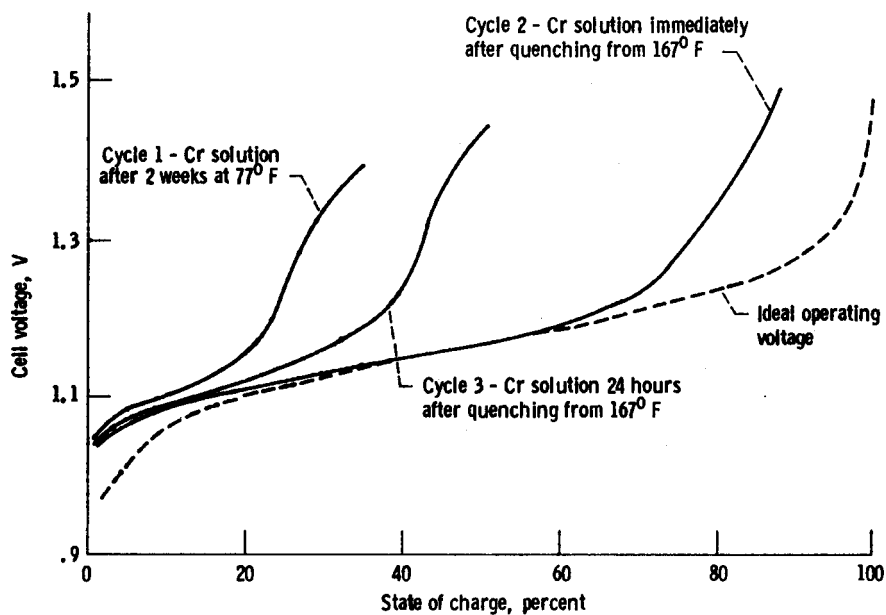


Figure 11. - Constant-current charge performance of iron-chromium Redox cell as a function of chromium reactant history. Current density, 21.5 mA/cm<sup>2</sup>.

Although this heating-quenching mode of operation is not applicable on a system basis, it demonstrated the performance that can be expected from a pentahydrate-rich chromium solution.

### Life (Endurance) Tests

Long-term testing of single cells is necessary to determine whether any life-limiting processes are proceeding within the cells. Such processes could be the result of either physical, chemical, or electrochemical attack on cell components. This type of testing was done on 14.5-cm<sup>2</sup> and 320-cm<sup>2</sup> Redox cells. Generally, the cells were repetitively cycled between depth-of-discharge (DOD) limits of 10 percent and 90 percent, at some nominal current density. These cycles could be normal or accelerated, the latter resulting from turning off the reactant pumps and limiting the capacity to the quantity of reactant trapped within the cell. In this mode fresh solutions occasionally were pumped into the cell to prevent the magnification of reactant crossmixing effects. The cell was charged or discharged periodically to 50-percent DOD and polarization data (voltage versus current density), both charging and discharging, were obtained. Any change in polarization characteristics over time indicates an aging process. The nature of the change indicates which component of the cell is being affected.

During normal cycles the variation of open-circuit voltage as a function of SOC was monitored. The degree of hysteresis between the charge and discharge portions of these data is a measure of the ability of the chromium electrode to catalyze the reaction rate of, or the equilibrium rate between, the various Cr<sup>+3</sup> complexes present (as discussed in a preceding section).

The rate of hydrogen evolution from the chromium electrode was also monitored by oxidizing the hydrogen electrochemically against FeCl<sub>3</sub> in a rebalance cell and measuring the ampere-hours of charge transferred. Significant changes in this characteristic are generally related to the nature and activity of the chromium electrode catalyst.

An additional test, quite severe, was also occasionally used. It involves driving the Redox cell negative as much as 1 V and holding it there for an extended period. Subsequent polarization, cycling, and gas evolution data define the electrode stability. Another aspect of electrode stability manifests itself as a dip in the voltage-versus-time curve during a discharge at constant current. This dip is generally assumed to result from an initially incomplete deposition of gold on the carbon (or graphite) felt substrate, followed by lead deposition on both the gold and the bare felt. During discharge the lead deplates from the felt, and subsequent discharge performance reflects the poor catalytic activity of the felt.

Membrane resistivity was monitored periodically throughout the test, both from the slopes of the polarization curves and by measurement with a 1000-Hz bridge. A gradual increase in resistance indicated progressive fouling of the membrane, perhaps by materials being extracted from other cell components or by the ferric ion chloro complexes. Physical changes caused by chemical attack would eventually result in leakage paths through the membrane. Post-test analysis of the ion exchange capacity and the water content of the membrane were used to evaluate polymeric structural integrity.

The life testing of an improved chromium electrode in a 320-cm<sup>2</sup> single cell was completed in 1981 after 18 months of operation. Polarization test results during this period are shown in figures 12 and 13. The electrode was initially tested for catalyst stability by driving the cell into reversal and

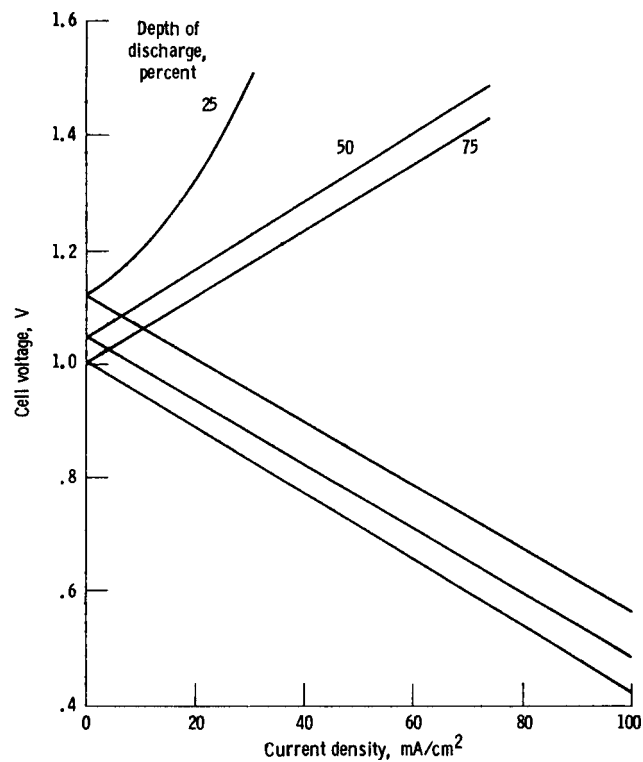


Figure 12. - Polarization performance of 320-cm<sup>2</sup> Redox cell after 18 months of standard and accelerated cycle testing. Ten cell reversals to -1.1-V open-circuit voltage; 20 000 rapid cycles; 10 changes of solution; 3000 full cycles with flowing solutions.

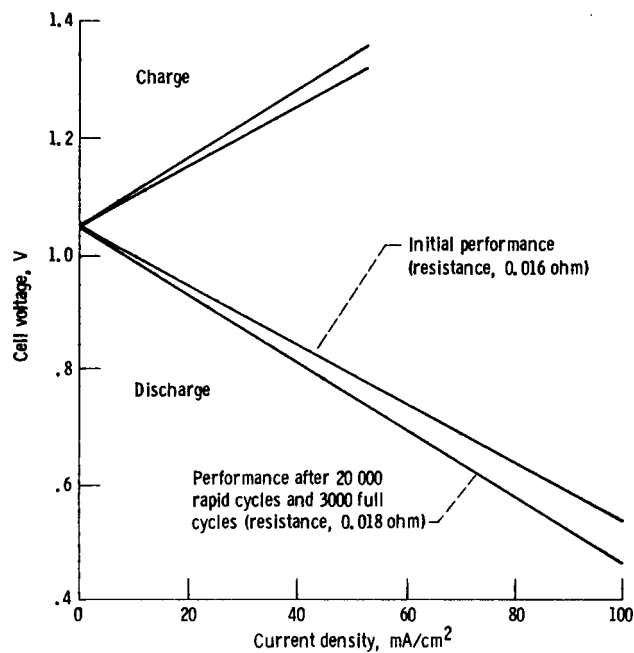


Figure 13. - Change in polarization performance of 320-cm<sup>2</sup> Redox cell during 18 months of standard and accelerated cycle testing.

holding until a negative open-circuit voltage was established. (This was possible because of a small amount of reactant crossmixing.) Chromium electrode performance was not affected by this severe electro-oxidative condition. The cell was then charged and discharged through 20 000 accelerated cycles, between approximately 10-percent and 90-percent DOD, with no significant change in performance. After the accelerated cycles 3000 full cycles with flowing reactants were accumulated with no changes in electrochemical activity. These results demonstrate that stable, long-life chromium electrodes can be prepared.

### Iron-Hydrogen Rebalance Cell

There are several ways in which the reactants of a Redox system can become chemically out of balance, so that there is a difference between the effective states of charge of the two fluids. Intrusion of air (oxygen) into either reactant system is one way. Another is the generation of hydrogen at the chromium electrode because of faulty catalyst application. Either of these situations leaves the iron solution in a higher SOC than the chromium solution. The rebalance cell electrochemically reduces the excess ferric (charged) iron to the ferrous state, consuming hydrogen in the process. If air intrusion is the cause of imbalance, the necessary hydrogen must be supplied externally. Otherwise the hydrogen evolved at the chromium electrode is used to carry out the rebalancing. In either case the use of an ampere-hour integrator in conjunction with the iron-hydrogen rebalance cell provides an analytical method for quantitatively measuring the degree of chemical imbalance. In the rebalance cell the iron half-cell contains a rigidized carbon felt electrode. The original hydrogen half-cell design consisted of a platinized, wetproofed carbon paper electrode and a porous carbon felt or graphite felt support structure that also served to distribute the incoming hydrogen to the electrode.

Until recently, the performance of the rebalance cells, defined as the short-circuit current when supplied with 1.0 M  $\text{FeCl}_3$  solution and 2- to 3-psig hydrogen, tended to decrease on a day-to-day basis. Periodic flushing with 1.0 M  $\text{H}_2\text{SO}_4$  was required to restore the original levels of performance.

A recent change in the configuration of the rebalance cell greatly improved performance. The carbon felt that was used as the hydrogen diffuser was replaced with reticulated vitreous carbon (RVC). Both a radiation-grafted polyethylene membrane from RAI Research and the standard Ionics CD1L membrane were used. A sketch of the improved rebalance cell configuration is shown in figure 14. Typical performance for this configuration is shown in figure 15. Reproducible performance was obtained for a period of several months with this configuration, using both types of membranes. However, experience with the experimental RAI membrane showed less iron fluid transfer than with the Ionics membrane. Apparently the main reason for the improved and more consistent performance was reduced flooding at the electrode-RVC interface. Fluid retention, which would prevent hydrogen from reaching the electrode, did not occur.

### Premixed Reactants

The ability to operate Redox cells with totally mixed reactants would offer many advantages to the Redox system. By definition, crossmixing of reactants would no longer be a factor. Microporous separators could be used, offering significantly lower cell resistance and cell cost. Also, any tendency toward solvent transfer could be countered easily by applying pressure or simply by pumping fluid back to the diminished reservoir.

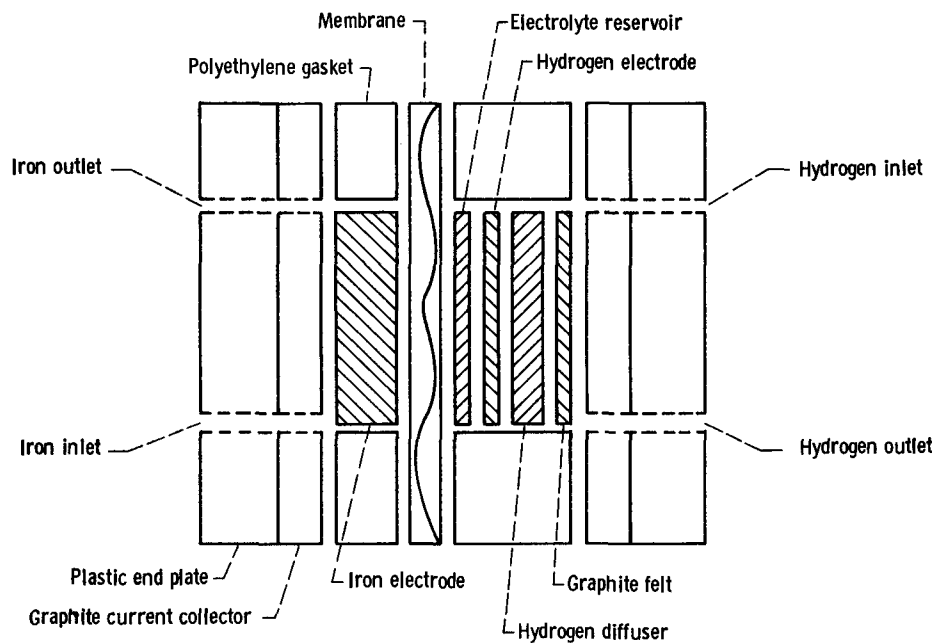


Figure 14. - Configuration of Improved iron-hydrogen rebalance cell.

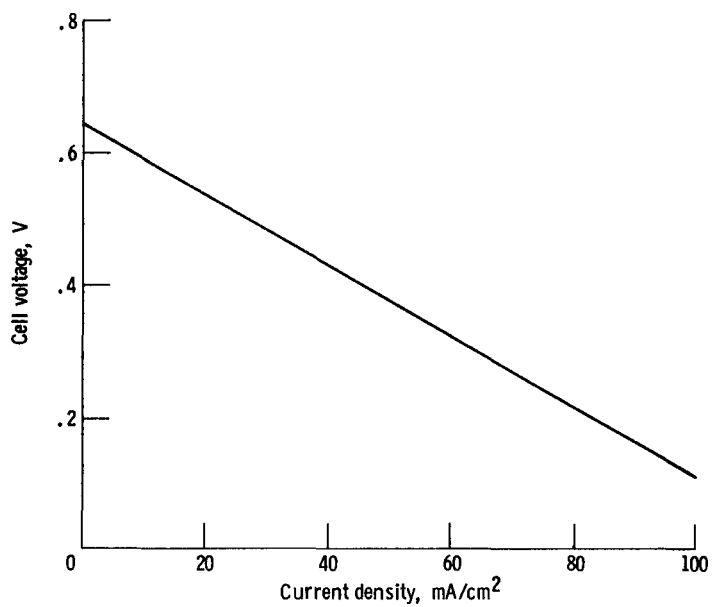


Figure 15. - Polarization curve for improved rebalance cell: hydrogen pressure, 2 psig; 1.0 molar  $\text{FeCl}_3$  in 1.0 N HCl; cell area, 14.5 cm<sup>2</sup>; single cell.

Electrochemically there should be little effect of using mixed reactant solutions. Iron present in the chromium solution remains passive as ferrous ion through both charge and discharge. Chromium in the iron solution remains in the trivalent oxidation state during cycling. The major disadvantage is the larger quantities of reactant chemicals required. However, the higher system chemical costs would be offset to some degree by cost reductions for membranes and for solution maintenance. In addition, as discussed in a later section, contract studies of the cost of the iron and chromium reactants, when produced in large quantities, show the projected costs to be much lower than previously estimated.

Some experimental work has been done, the objective of which was to demonstrate the feasibility and advantages of the mixed-reactant concept. Mixed solutions containing approximately 1 molar active species were tested in a 14.5-cm<sup>2</sup> single-cell system with a microporous separator. Cell performance was evaluated by monitoring internal resistance, electrode reversibility, polarization characteristics, and hydrogen evolution rates. Performance was optimized by heating and quenching the negative "chromium" solution in order to obtain a pentahydrate-rich reactant. Through the quenching technique, excellent charging was achieved to greater than 90-percent SOC, especially with the low-resistance Daramic microporous membrane.

For comparison, figure 16 shows the polarization curves for a Daramic microporous membrane with mixed reactants and for a standard Ionics CD1L membrane with unmixed reactants. The lower resistance of the porous membrane resulted in less cell polarization, which would lead to an improved round-trip voltage efficiency. The linearity of the polarization curves indicates electrode reversibility with the mixed reactants. Figure 17 compares the constant-current charging performance with mixed reactants for both the standard membrane and the Daramic porous membrane. Again, a significant reduction in cell resistance was noted with the porous membrane. However, this was accompanied by a reduction in ampere-hour efficiency, from 95 percent to 84 percent, due to self-discharge through the porous membrane.

Overall, the results of this experimental evaluation during the reporting period were encouraging and the work is continuing.

#### Four-Tank Operation

In the present iron-chromium Redox system configuration, two tanks, one per reactant solution, are used. Each fluid flows at some rate greater than the stoichiometric requirement, is charged or discharged as it passes through the working cell (or cells), and then returns to the tank and is mixed with less-reacted material. This continuous mixing of solutions at different states of charge results in changes in the effective reactant activities such that discharge voltages (at constant current) continuously fall and charge voltages rise. The net result is a reduction of system efficiency. Some of this loss can be avoided by using two tanks for each solution, one acting as a receiver for the partially spent reactant leaving the cell (or cells). Discharge, for example, would then proceed in constant-voltage steps: as one tank was emptied, flow would be reversed and discharge would then be resumed at a lower constant voltage.

This concept was successfully evaluated in the laboratory with a 320-cm<sup>2</sup> cell. Figure 18 compares the experimental two-step constant-current discharge with a four-tank system and the calculated performance of a

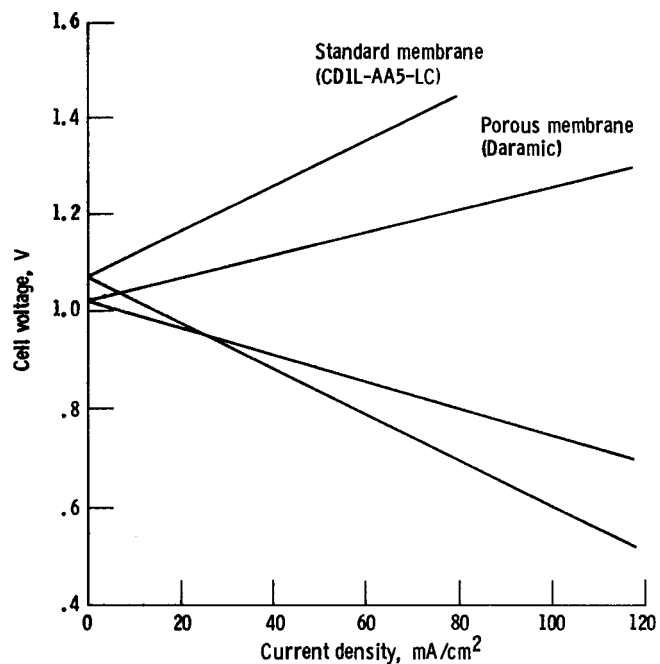


Figure 16. - Charge and discharge polarization curves for iron-chromium Redox cells. Comparison of a standard ion-exchange membrane and unmixed reactants with a commercial microporous membrane and mixed reactants. Chromium reactant heated to 167° F and then quenched to 77° F; state of charge, 50 percent.

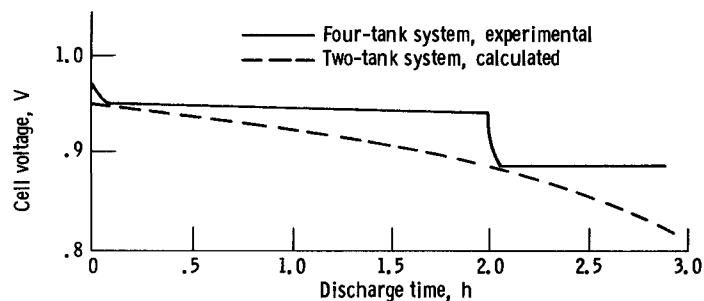


Figure 18. - Measured constant-current discharge performance of a four-tank Redox system, compared with calculated performance for a two-tank system. Current density, 14 mA/cm<sup>2</sup>; flow rate, 1.5 times stoichiometric; cell area, 320 cm<sup>2</sup>; single cell.

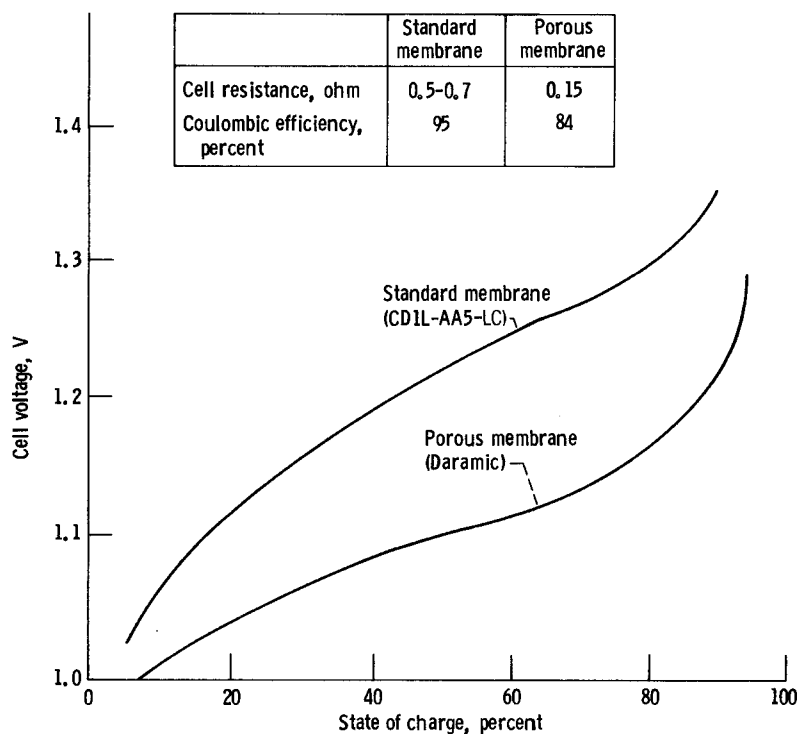


Figure 17. - Constant-current charging performance with mixed reactant solutions. Comparison of a standard ion-exchange membrane and a commercial microporous membrane. Chromium reactant heated to 167° F and then quenched to 77° F; current density, 21.5 mA/cm<sup>2</sup>.



corresponding two-tank system. Obviously the time-averaged discharge voltage for the two-step discharge is significantly greater than the average voltage for the continuous discharge. Preliminary analyses indicate that the four-tank concept could improve system round-trip energy efficiency by 3 to 5 percentage points and slightly reduce the system cost.

## ELECTRODE DEVELOPMENT

Redox flow cell performance is significantly affected by the electrochemical characteristics of the electrodes. The requirements for a reversible iron electrode (note throughout that generally a phrase such as "iron electrode" refers to the solid, electron-conducting material at which the iron redox reactions occur) have been met satisfactorily by using an uncatalyzed carbon felt. However, theory and experience have shown that a lead-gold catalyst is needed for the chromium electrode to increase the rates of chromium reduction and oxidation and to provide a hydrogen evolution overpotential. Thermodynamically hydrogen should be evolved before chromium is reduced. Appreciable coevolution of hydrogen not only reduces the coulombic efficiency of the system, but, over a period of many cycles, allows the system to become chemically out of balance and thus lose effective capacity.

The performance of carbon felt chromium electrodes depends on the production history of the felt, the cleaning procedure, any surface activation treatment, and the methods of deposition of the gold and lead. The most significant aspect of the felt production process is the temperature at which the precursor, usually rayon felt, is carbonized and to some extent graphitized. The relationship between this temperature and the performance of resultant electrodes has been evaluated.

The ability to prepare catalyzed felt chromium electrodes reproducibly also has been examined, by comparing the performance of identically prepared samples. In addition, the possibility of doing away entirely with the felt electrode structures has been evaluated, using instead planar electrodes, both gold catalyzed and uncatalyzed but roughened.

Under contract, Giner, Inc., used cyclic voltammetry and electron microscopy to characterize felt chromium electrodes. An effort also was begun to optimize the catalysis procedure for these electrodes.

### Carbon Felt Processing Temperature

A systematic study was undertaken to produce carbon felts at various processing temperatures and to evaluate them as substrates for catalyzed chromium electrodes. Carbon felt samples, prepared at six processing temperatures, from both "as received" and "solvent cleaned" lots of rayon felt, were purchased from Fiber Materials, Inc., where the production process was closely monitored. The locations on the roll at which samples were taken, sample thicknesses, heating rates, furnace conditions, and handling were tightly controlled. A small quantity of the rayon precursor was solvent cleaned (scoured) to remove sizing and any possible organic contamination before further processing along with the unscoured material.

A large roll of the rayon precursor was first pyrolyzed at 700° to 800° C. After pyrolysis the roll was divided into samples for each specific graphitization run. A small induction furnace was used for heating each

sample to the desired final temperature. All heating operations were done under a nitrogen atmosphere. The final temperatures chosen to produce felt samples with increasing degrees of graphitization were 1250°, 1350°, 1500°, 1650°, 1800°, and 2300° C.

Catalyzed chromium electrodes were prepared from each of the samples by using the standard cleaning and catalysis technique: felt samples were heated in 45 percent KOH for 1 h at 90° C, rinsed thoroughly, and damp dried. The dampened samples were then soaked in an alcoholic gold chloride solution to provide the desired gold loading of 12  $\mu\text{g}/\text{cm}^2$ . After drying at 100° C, the samples were heated to 270° C for 2 h to complete thermal decomposition of the gold salt. The lead component of the chromium electrode catalyst was provided after the electrode was incorporated into a complete Redox cell by adding saturated lead chloride solution to the chromium reactant solution. Electrochemical plating of the lead onto the thermally deposited gold completed the catalysis.

Twelve electrode samples were tested in 14.5-cm<sup>2</sup> single-cell systems (six temperature variations each, for the scoured and unscoured precursors). Cumulative hydrogen evolution was measured as a function of SOC and is shown in figure 19 for the unscoured and scoured samples, respectively. The general trend for both sets of samples was for decreasing hydrogen evolution as the processing temperature increased. Polarization data for all samples were virtually identical. Results of the constant-current charging indicated better activity for chromium reduction on the lower temperature felts; however, these felts also had greater hydrogen evolution activity.

Catalyst stability was evaluated by driving each cell in discharge to a negative open-circuit voltage and then monitoring performance during the subsequent standard cycle. (A negative open circuit is attainable because of traces of reactants cross diffused across the cell membrane.) A resultant increase in hydrogen evolution and a "dip" in the constant-load voltage during discharge were observed primarily on felts processed at 1500° C and below. This probably indicates that an irreversible change in the gold-lead catalyst morphology occurred during cell reversal.

From the results of this testing program the 1800° and 2300° C processing temperatures seem to give the best overall performance.

### Chromium Electrode Reproducibility

Four 320-cm<sup>2</sup> gold-catalyzed chromium electrodes were prepared from the same carbon felt lot by using identical cleaning and catalysis procedures for each. Adjacent felt samples from across the width of the carbon felt roll were used. Each sample was individually cleaned and catalyzed with 12.5- $\mu\text{g Au}/\text{cm}^2$ . The catalyzed chromium electrodes were then evaluated in 320-cm<sup>2</sup> single cells for hydrogen evolution, chromium reduction activity, and catalyst stability. Performance characteristics of all four electrodes were very similar.

Hydrogen evolution was monitored while charging each cell to 75-percent SOC, with an upper voltage limit of 1.25 V. Below 60-percent SOC no hydrogen was detectable. Between 60-percent and 75-percent SOC there was visual evidence of hydrogen evolution but at a low rate. There was excellent consistency among these observations for the four electrodes. Electrode performance reproducibility in terms of chromium reduction was evaluated by monitoring cell voltage during charging at a constant current of 21.5 mA/cm<sup>2</sup>. Graphical results for the four cells are shown in figure 20. The SOC at which the cell voltage increased rapidly due to depletion of the chromic pentahydrate species

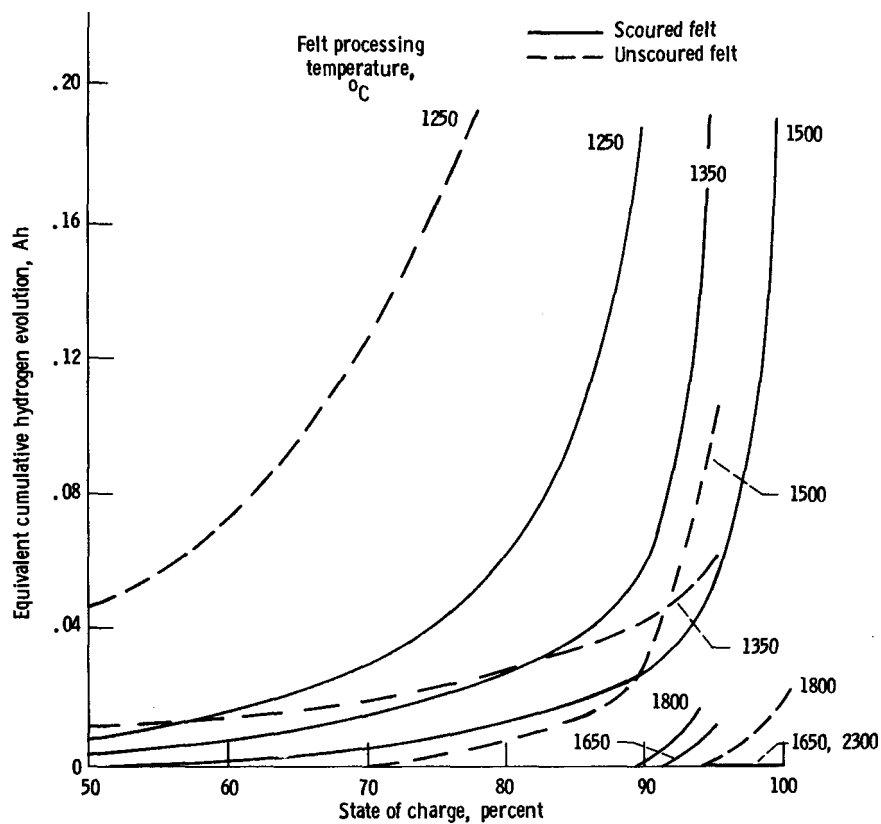


Figure 19. - Hydrogen evolution from graphitized felt chromium electrodes, during charge, as a function of felt processing temperature. Charge at  $21.5 \text{ mA/cm}^2$ , taper to 1.25 V.

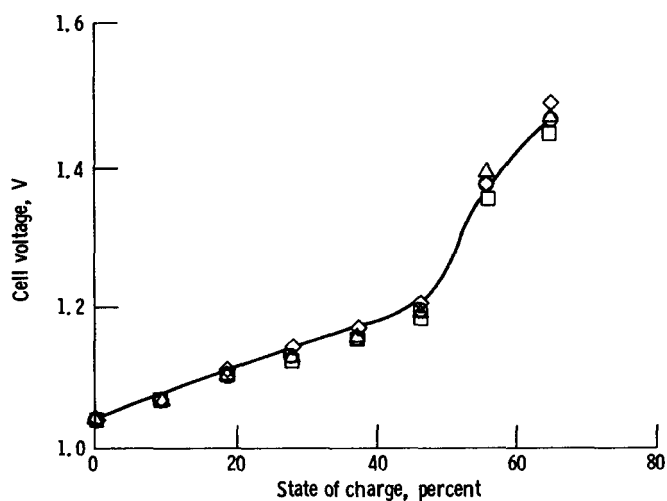


Figure 20. - Reproducibility of chromium electrode preparation. Constant-current charging of four cells with separately prepared chromium electrodes. Current density,  $21.5 \text{ mA/cm}^2$ .

is a measure of the electrode's reactivity for reducing the chromic solution. At voltages above 1.4 V the major cathodic reaction was hydrogen evolution. The SOC's at which all four electrode showed rapid voltage rise (50 percent to 55 percent) were very consistent.

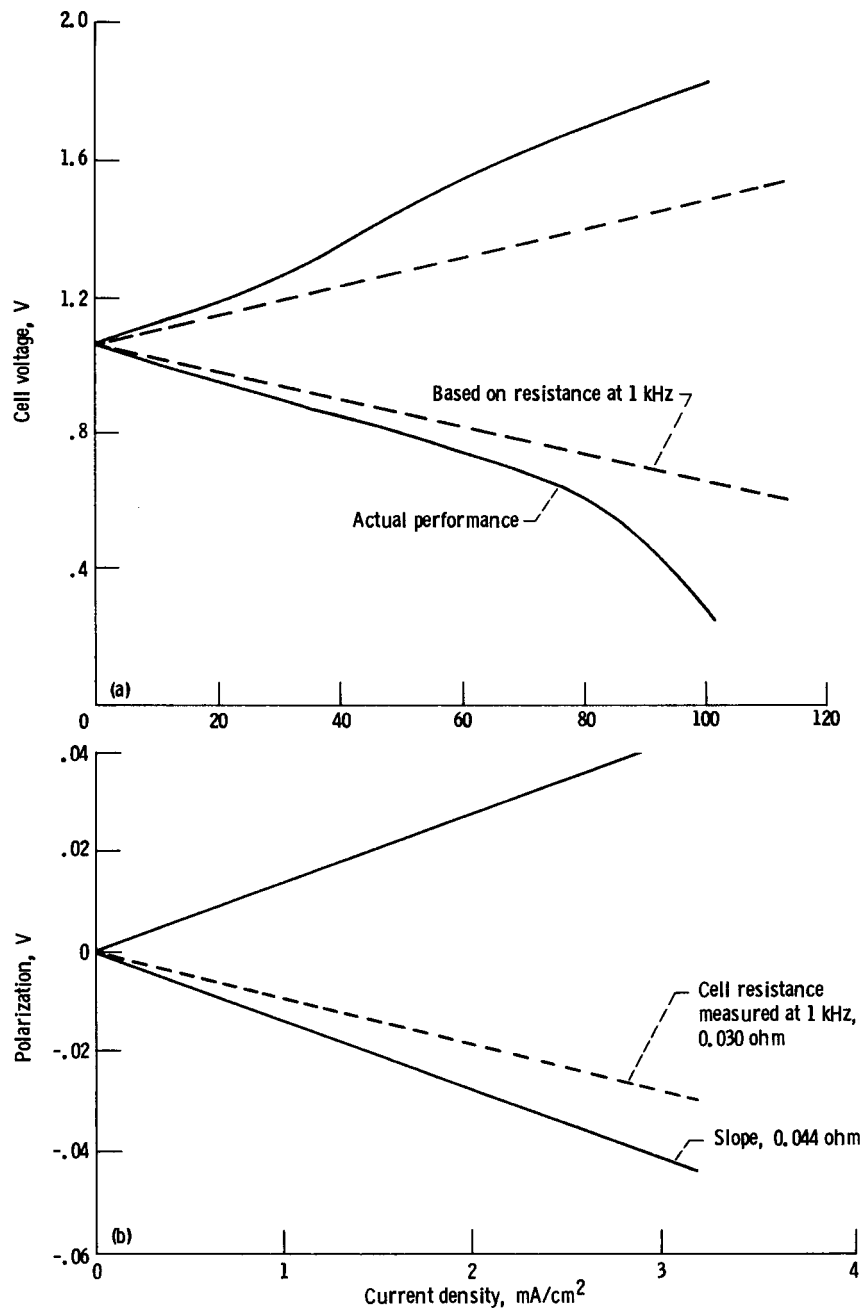
Catalyst stability of each electrode was determined by impressing a negative voltage on the cell in order to place the chromium electrode under electro-oxidative conditions. After cell reversal, hydrogen evolution and chromium reduction were again monitored during a constant-current cycle. No measurable or observed change in either characteristic indicated good catalyst stability for all four electrodes.

Another evaluation of catalyst stability was based on cell performance during discharge into a constant resistive load. The occurrence of a cell voltage dip (part way through the discharge) is interpreted as the result of lead deplating from regions that have lost the underlying gold catalyst. No such voltage dips were observed before or after the reversal cycles, indicating that the gold catalyst had been successfully applied to all four electrodes and was not readily removed by electro-oxidation.

Results of these studies, although limited, demonstrate that catalyzed chromium electrodes with good performance can be made reproducibly. An in depth statistical approach would be needed to critically evaluate a carbon felt lot for uniformity and catalyzed electrodes for catalyst application reproducibility.

### Planar Electrodes

Relatively early in the Redox project it was found that the polarization curves for iron-chromium Redox cells with graphite felt electrodes were straight lines, out to discharge rates as great as  $1000 \text{ mA/cm}^2$ . Among other things, this fact revealed the excellent mass transport environment within the felt structure and raised the question of whether electrodes with much less surface area might perform adequately at reasonable current densities. Initial laboratory tests were carried out with  $14.5\text{-cm}^2$  cells from which the felt electrodes had been removed, leaving the flat surfaces of the machined carbon current collectors to act as electrodes. The collector for the chromium half-cell was catalyzed in the standard way. Discharge polarization performance, as shown in figure 21(a), was linear out to 60 or  $70 \text{ mA/cm}^2$ . However, the slope of the linear portion of the data was greater than the cell resistance measured with an ac bridge at 1000 Hz. This discrepancy was also observed with a  $320\text{-cm}^2$  cell of the same construction, which was used for a closer examination of the low-current-density end of the discharge curve (fig. 21(b)). The discrepancy was assumed to be the manifestation of a linear component of kinetic polarization. The final evaluation of the use of planar electrodes consisted of a repeat of the test with the  $320\text{-cm}^2$  cell after first increasing the electrode surface areas an estimated 65 percent by roughening with sandpaper. The chromium electrode was not recatalyzed after this treatment; yet cell performance, shown in figure 22, was significantly improved. The discrepancy between the measured cell resistance and the slope of the polarization curve was reduced about 50 percent. Since, in the absence of the felt electrodes, current conduction between the current collectors is totally ionic, the measured cell resistance at 1000 Hz for the planar electrode configuration was about twice that for a conventional cell. This tends to further reduce the potential attractiveness of cells with planar electrodes, but only a trade-off analysis giving consideration to total system cost, efficiency, ease of manufacture, etc., will give a definitive resolution to the question.



(a) 14-cm<sup>2</sup> cell; 50-percent depth of discharge.  
 (b) 320-cm<sup>2</sup> cell; 50-percent state of charge.

Figure 21. - Polarization performance of iron-chromium Redox cells with planar electrodes.

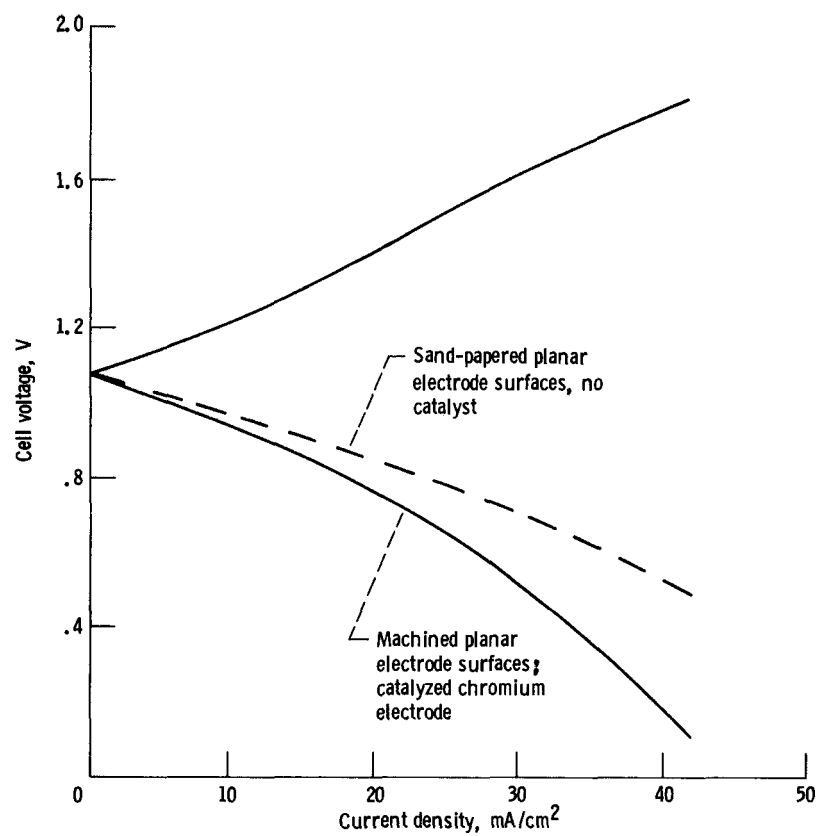


Figure 22<sub>2</sub> - Effect of surface roughening on planar electrode performance. Cell area, 320 cm<sup>2</sup>; single cell.

## Giner, Inc.

During the first half of 1981, Giner, Inc., completed their contract effort by using electrochemical analytical techniques such as cyclic voltammetry to characterize and evaluate catalyzed carbon felt or graphite felt electrodes for chromium redox reactions (ref. 4). This work closely paralleled the previously discussed work at NASA Lewis, which was carried out in complete iron-chromium Redox cells. However, the contract effort has provided a more detailed examination of catalyst type and loading and felt processing temperature, in terms of activity for the chromium redox reactions and hydrogen evolution.

The effect of catalyst loading on electrode performance was evaluated by using three felts from Fiber Materials, Inc.: 3.2-mm-thick carbon felt, 3.2-mm-thick graphite felt, and 6.4-mm-thick carbon felt. The standard method of gold application, starting with gold chloride solutions in dilute methanol (ref. 5), was used. The lead was then applied electrochemically from the test solutions, which contained various lead chloride concentrations. In general, hydrogen evolution increased with gold loading, but in varying degrees for each type of felt. There also appeared to be a correlation between the  $\text{Cr}^{+2}$  oxidation activity and the amount of lead plated on the electrode during the previous cathodic sweep, which is in turn proportional to the solution concentration of lead. This seeming correlation probably arises because, with higher lead solution concentrations, the lead plates at a more positive voltage and thus does not compete with the chromium reduction at the more electronegative potentials of the cathodic sweep. More chromium gets reduced and is thus available for subsequent oxidation.

As at NASA Lewis, FMI felts processed at 1250°, 1500°, 1650°, and 2300° C were evaluated as chromium electrode substrates. Initial electrochemical measurements revealed an apparent correlation of the hydrogen evolution rate and chromium redox reactions with processing temperature. Both decreased with increasing processing temperature. Felt processed at 1650° C seemed to give the optimum trade-off between these two characteristics. Physical and electrochemical characterization of this series of felt samples will be carried out in a future program.

Several alternative catalyst systems were also investigated and compared with the standard gold-lead system. These were the silver-lead, silver-bismuth, and gold-bismuth combinations. The silver-lead system performance was similar to the gold-lead system performance except that the hydrogen overvoltage appeared more favorable. The disadvantage of the silver catalyst is that the lower reduction potential for silver in HCl (~ 0 V versus standard calomel electrode (SCE) as compared with gold at 0.8 V versus SCE) means it would be a less stable catalyst during discharge.

Promising results were obtained by using bismuth with both silver and gold. The reduction potential for bismuth is more electropositive than that for lead, and this makes it a more stable catalyst component than lead, which oxidizes near the chromium electrode standard potential. Therefore while lead tends to deplete from the electrode at low SOC, typical cell cycling would not cause bismuth to go into solution during discharge. This possible advantage of the gold-bismuth system will be evaluated at NASA Lewis in complete Redox cells.

An attempt was made to correlate the distribution of the gold catalyst component within felt electrodes and the performance of those electrodes. Transmission electron microscopy was used to measure the gold distribution, and energy dispersive analysis by X-ray (EDAX) was used to verify the gold.

Bare carbon felt surfaces were found to be quite smooth and relatively free of particles or roughness. Carbon felts that had been catalyzed with 12.5, 25, and 50  $\mu\text{g}/\text{cm}^2$  of gold showed clearly visible particles on the surface that were identified as gold by EDAX analysis. Examination of the gold particle size distribution gave some correlation with activity for the chromium redox reactions. In general, better performance was obtained from electrodes with small gold particle size. As a matter of fact, gold particles could not be detected on samples of electrodes that had been prepared at NASA Lewis and that had shown good chromium activity and low hydrogen evolution. The conclusion to be reached is that "clumping" of the gold, either in application or during use, will result in a degradation of electrode performance.

## MEMBRANE DEVELOPMENT

From the standpoint of Redox cell performance, the properties desired in a conventional Redox cell membrane are a high selectivity combined with a low resistivity. The former characteristic requires a near-total rejection of the reactant iron and chromium ions and their various complexes. The latter property requires free passage of the chloride counter-ions and hydrated protons to carry the current and to sustain charge neutrality. The seeming conflict between these requirements calls for subtle control of the membrane charge density and "pore size" so that the larger, generally positively charged reactant ions and complexes are excluded while the negative chloride ions and the hydronium ions easily pass through. Membrane thickness also can be a significant factor in determining membrane properties.

Other important membrane characteristics that are unrelated to cell performance are ease of manufacture, yield, mechanical strength, amenability to scale-up, operational life, and cost.

The membranes being used most commonly in the Lewis Redox flow cells have been developed by Ionics, Inc., and consist of a polymerized anion exchange resin reinforced by a thin substrate of woven fabric. The resin is a copolymer of vinylbenzyl chloride (VBC) and dimethylaminoethyl methacrylate (DMAEMA), which form the backbone and crosslink components, respectively. The substrate is a calendered modacrylic woven fabric. By varying the following parameters a wide selection of membrane characteristics is possible:

- (1) Backbone monomer density and type
- (2) Crosslink monomer density and type
- (3) Fraction of nonpolymerizable material (NP content) in the membrane precursor
- (4) Amount of polymerizing catalyst
- (5) Total membrane thickness (different substrate materials or processing)
- (6) Amount of functionality (addition of functional groups and sites in polymer structure).

As mentioned above, the membrane development portion of the Redox project was carried out under contract by Ionics, Inc., with NASA Lewis providing direction. For membranes that have attractive characteristics based on initial screening at Ionics, Inc., NASA Lewis performs more-detailed evaluations and in-cell tests. The following describes the developments during 1981.



# Ionics, Inc.

The membrane development program was begun in 1974 at Ionics, Inc., and has completed its fourth follow-on phase. During this reporting period (December 1980 - December 1981; contract DEN3-204), efforts were concentrated on resistivity and selectivity improvement, cost reduction, and fabrication of scaled-up membranes. At the end of the reporting period the best membrane remained the one that was the standard at the start of the period, CD1L-AA5-LC (27.5 NP), which has the following characteristics:

Backbone . . . . .	Vinylbenzyl chloride (VBC)
Crosslinker . . . . .	Dimethylaminoethyl methacrylate (DMAEMA)
Catalyst concentration, percent . . . . .	0.0625
Nonpolymerizable content, percent . . . . .	27.5 iso-butanol
Substrate . . . . .	Woven, calendered modacrylic fabric; multifilament thread
Backbone-crosslinker ratio . . . . .	1/2
Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup> . . . . .	4.2
Water content, percent . . . . .	34.8
Ion exchange capacity (IEC), milliequivalents/ dry gram (meq/dg)	
Strong . . . . .	1.93
Weak . . . . .	2.32
Total . . . . .	4.25
Thickness, cm . . . . .	0.04
Selectivity, $\mu\text{g Fe}^{+3}/\text{h-cm}^2\text{-M/liter}$ . . . . .	~20

The major effort this year to improve this membrane was to reduce the resistivity by varying the nature and reducing the thickness of the supporting substrate. The variables considered included chemical composition (polyethylene, polypropylene, modacrylic, polyester), fabrication (woven, nonwoven, monofilament versus multifilament thread), thickness, fabric weight, porosity, surfactant pretreatment, calendering, and laminating. With few exceptions all of the candidate substrates were formed into membranes by using the standard CD1L formulation. The screening criteria generally were the measured resistivity in 0.1 N HCl and the results of dye tests to check the bond between substrate and ion exchange resin.

Table 1 compares fabrics woven of polypropylene multifilament yarns. Only the 14-by-14 (threads per inch) fabric shows a lower resistivity than the standard CD1L. Table 2 compares nonwoven fabrics of polypropylene and polyester. The candidates showing attractive resistivities generally did so because of poor adhesion of resin to the substrate. Nonwoven polyethylene (table 3) membranes not

TABLE 1. - EFFECT OF SUBSTRATE WEAVE ON CD1L-AA5-LC MEMBRANE CHARACTERISTICS: POLYPROPYLENE MULTIFILAMENT YARNS

Construction	Fiber thickness, mm	Membrane thickness, mm	Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	Dye test
20x16 Scrim	0.50	0.66	4.7	Good ↓
10x18 Scrim	.45	.66	4.6	
20x20 Scrim	.50	.62	4.8	
17x17 Scrim	.50	.67	4.7	
14x14 Scrim	.45	.57	3.9	

TABLE 2. - EFFECT OF SUBSTRATE MATERIAL ON CD1L-AA5-LC MEMBRANE CHARACTERISTICS: NONWOVEN FABRICS

Construction	Membrane weight, g/m <sup>2</sup>	Membrane thickness, mm	Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	Dye test
Oriented polyester, calendered on one side	----	0.55	7.3	Poor ↓
Oriented polyester, calendered on one side	----	.95	5.8	
Oriented polypropylene, calendered on one side	65	.33	3.3	
Oriented polypropylene, calendered on one side	111	.55	4.2	
Random polypropylene point seal (hot dot)	35	.43	2.6	Good - spalls slightly
Random polypropylene point seal	39	.26	2.0	Poor
Random polypropylene point seal	49	.38	2.5	Poor
Random polypropylene point seal	97	.70	4.3	Good - spalls slightly
Unidirectional polypropylene, heavily calendered on one side	52	.23	3.7	Fair - spalls

only exhibited low resistivities, but also were less efficient than the standard in excluding ferric ions. In table 4, where laminates of nonwoven polypropylene are compared with the standard, several had similar selectivities and lower resistivities. However, the range of resistivities being sought was 2.5 ohm-cm<sup>2</sup> or less.

Several substitutions for the standard nonpolymerizable (NP) solvent, iso-butanol, were evaluated. To the degree to which the NP solvent affects the polymerization process, varied membrane properties, such as resistivity and selectivity, can be expected. Membranes prepared with several levels of Cellosolve (ethylene glycol monoethylether) and, because of its low free-radical chain-transfer properties, n-butanol, are compared in table 5. Again, no clear-cut superiority was shown over the standard CD1L membranes. In addition to the variations presented in table 5, 0.25 n-butanol and bis [2-(2-methoxymethoxy) ethyl] ether (B2MEEE) were also evaluated but gave very poor, cracked, leaky products.

In an endeavor to increase the ion exchange capacity of the experimental membranes, and thereby their selectivity, formulations were prepared in which the usual ratio of 2 parts DMAEMA to 1 part VBC was varied to favor the VBC content. The reasoning was that the pendant-CH<sub>2</sub>Cl groups from the excess VBC could be quaternized to give high "strong" ion exchange capacity (IEC) in acid solutions. As shown in table 6, the resultant membranes had IEC's very close to the theoretical. However, they were "tight" and had relatively low water content, leading to high resistivities. Also, in production the leak-free yield was low.

Because of rapid increases in the cost of VBC, its replacement in the membrane formulation with dichloroxylene (DCX) has been attempted. Low solubility of the resulting resin adduct in the standard iso-butanol required evaluation of other NP solvents, tetrahydrofuran, t-butyl alcohol, isopropyl alcohol, dimethylformamide (DMF), and methanol/DMF. The product membranes had high water content, low molecular weight, and low crosslink density and tended to spall in salt or acid solutions. This work continues, seeking a solvent that will provide adequate monomer solubility and lead to a higher crosslink density.

Another approach to membrane modification was to use polymerization catalysts of greater and lesser activity than the standard. The intent was to alter the quaternization/polymerization sequence and thus the membrane properties. Table 7 again shows some membranes with acceptable properties; but in none do the combined values for resistivity and selectivity evidence a significant improvement over the standard CD1L.

Scaled-up standard CD1L membranes with a 95 percent yield of leak-free product were successfully produced. Five of these 107-cm by 51-cm membranes were sent to NASA Lewis for further evaluation. (The previous maximum size for CD1L membranes was 51-cm by 46-cm.) Measured selectivity, resistivity, and other characteristics for these membranes were normal for the standard formulation.

Some of the electrochemical transport properties of the CD1L-AA5-LC (27.5 NP) membranes have been measured. With 0.6 N HCl on each side, the water transport rate  $t$  was 71 milliliters per faraday. With 0.6 N HCl on one side and 1.2 N HCl on the other the transference numbers were:  $t_{Cl^-} = 0.64$  and  $t_{H_3O^+} = 0.36$ .

One membrane from a stack of 320-cm<sup>2</sup> Redox cells operated at NASA Lewis for over 3000 h was returned to Ionics, Inc., for recharacterization. As shown in table 8, there was no significant change in the physical properties of the membrane during the period of use.

Further details of the membrane development effort at Ionics, Inc., can be obtained in references 6 to 9.

TABLE 3. - CHARACTERISTICS OF CD1L-AA5-LC MEMBRANES WITH NONWOVEN POLYETHYLENE SUBSTRATES

Construction	Membrane thickness, mm	Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	Total ion exchange capacity, meq/dry g	Strong ion exchange capacity, meq/dry g	Water content, percent	0 to 24 h	24 to 28 h
						Iron selectivity, $\mu\text{g Fe/h-cm}^2\text{-M/liter}$	
Typical calendered modacrylic	0.40	4.3	3.76	2.05	37.6	23.0	----
Nonwoven polyethylene (no. 7)	.30	3.2	----	----	----	56.9	----
Nonwoven polyethylene (no. 7)	.36	4.4	<sup>a</sup> 3.86	<sup>a</sup> 2.01	<sup>a</sup> 36.8	50.4	----
Nonwoven polyethylene (low binder)	.34	3.6	4.05	2.49	32.3	30.0	28.9

<sup>a</sup>Determined on control membrane (calendered modacrylic).

TABLE 4. - CHARACTERISTICS OF CD1L-AA5-LC MEMBRANE WITH SUBSTRATE LAMINATES OF NONWOVEN POLYPROPYLENE

Construction	Membrane thickness, mm	Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	Total ion exchange capacity, meq/dry g	Strong ion exchange capacity, meq/dry g	Water content, percent	Iron selectivity, $\mu\text{g Fe/h-cm}^2\text{-M/liter}$
Calendered modacrylic control	0.40	4.6	3.98	1.85	30.5	26.3
Single-ply MBPP <sup>a</sup> (15594)	.22	2.3	----	----	----	149
Single-ply, 2.7-oz MBPP <sup>a</sup>	.76	3.7	4.03	1.95	36.4	23.1
Double-ply MBPP <sup>a</sup> (15592/15594)	.37	2.2	----	----	----	145
Double-ply MBPP <sup>a</sup> (15592/15592)	.28	3.0	----	----	----	49.7
Triple-ply, rough surface (91900/15592 <sup>a</sup> /91900)	.33	3.1	----	----	----	58.0
Double-ply MBPP 15592/15594 <sup>a</sup>	.38	3.0	----	----	----	48.8
15592 <sup>a</sup> /91900/15592 <sup>a</sup>	.45	3.2	----	----	----	28.4

<sup>a</sup>Melt-blown polypropylene.

TABLE 5. - CHARACTERISTICS OF CD1L-AA5-LC MEMBRANES WITH VARIATIONS IN STANDARD NONPOLYMERIZABLE SOLVENT CONTENT

Construction	Membrane thickness, mm	Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	Total ion exchange capacity, meq/dry g	Strong ion exchange capacity, meq/dry g	Water content, percent	0 to 25 h	24 to 28 h
						Iron selectivity, $\mu\text{g Fe/h-cm}^2\text{-M/liter}$	
Calendered modacrylic (27.5-NP n-butanol)	0.42	4.8	3.80	2.10	33.4	18.2	----
Calendered modacrylic (30-NP n-butanol)	.36	4.4	3.86	2.03	36.8	25.6	----
Calendered modacrylic (25-NP Cellosolve)	.39	5.3	4.37	2.15	32.5	18.8	----
Calendered modacrylic (27.5-NP Cellosolve)	.44	3.9	4.10	2.13	35.5	38.9	41.6
Calendered modacrylic (30-NP Cellosolve)	.38	4.6	4.25	2.09	37.6	53.7	----

TABLE 6. - CHARACTERISTICS OF CD1L-AA5-LC MEMBRANES WITH VARIATIONS IN STANDARD RATIO OF VINYL BENZYL CHLORIDE TO DIMETHYLAMINOETHYL METHACRYLATE

Characteristic	Mole ratio VBC/DMAEMA		
	2/1	1.5/1	1/1
Nonpolymerizable (NP) content	27.5	27.5	27.5
Resistance in 0.1 N HCl, ohm-cm <sup>2</sup>	20.7	7.9	5.7
Membrane thickness, mm	0.34	0.34	0.34
Ion exchange capacity, meq/dry g:			
Total	2.17	2.73	3.35
Strong	2.14	2.73	3.30
Weak	0.03	0	0.05
Water content, percent	26.2	35.6	38.8
Theoretical ion exchange capacity, meq/dry g:			
Total	2.17	2.60	3.24
Strong	2.17	2.60	3.24
Weak	0	0	0

TABLE 7. - CHARACTERISTICS OF CD1L-AA5-LC MEMBRANES WITH VARIATIONS IN STANDARD POLYMERIZATION CATALYST

Catalyst, percent	Membrane thickness, mm	Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	Total ion exchange capacity, meq/dry g	Strong ion exchange capacity, meq/dry g	Water content, percent	Iron selectivity, (1 M FeCl <sub>3</sub> /0.5 N HCl), μg Fe/h-cm <sup>2</sup> -M/liter
0.0625 V-52 (fast)	0.39	4.2	4.40	2.04	34.1	25.9
0.25 V-52	.41	5.0	4.50	2.17	34.0	19.5
0.5 V-52	.42	4.1	4.49	2.22	32.5	28.9
	.42					<sup>a</sup> 62.2
0.0625 L-82 (slow)	.45	3.4	4.17	2.34	43.7	131.4
0.25 L-82	.43	4.4	3.86	2.31	32.3	24.0
0.5 L-82	.45	4.6	4.19	2.15	33.8	28.1

<sup>a</sup>Iron selectivity test solution 1.5 M FeCl<sub>3</sub>/1 N HCl on one side and 1 N HCl on other instead of 1.0 FeCl<sub>3</sub>/0.5 N HCl and 0.5 N HCl.

TABLE 8. - PHYSICAL CHARACTERISTICS of CD1L-AA5-LC (27.5 NP) MEMBRANES BEFORE AND AFTER 3000-h TEST AT NASA LEWIS

[As returned, membrane was strongly acid and contained iron ions. It was washed, then analyzed.]

Characteristic	Initial	After 3000 h
Ion exchange capacity, meq/dry g:		
Total	4.25	4.28
Strong	1.93	1.83
Weak	2.32	2.45
Membrane thickness, mm	0.42	0.41
Resistivity in 0.1 N HCl, ohm-cm <sup>2</sup>	4.2	4.6
Water content (as received), percent	34.8	37.0

## NASA Lewis Research Center

The in-house work in the membrane area dealt primarily with the evaluation of membranes that were produced as a result of the Ionics, Inc., contracts. Selected membranes that had undergone preliminary tests at Ionics were sent for further evaluation and screening tests to Lewis. These tests consisted of

- (1) Dye testing for pinholes.
- (2) Static diffusion and selectivity tests - Small membrane samples are placed between half-cell chambers filled with various reactant solutions and are exposed to various temperature conditions. Periodically, solution is withdrawn and analyzed. Permeability of the membrane to the several species is then determined.
- (3) Area resistivity - Resistivity is determined in various reactant solutions at various temperatures. These measurements are under static (non-flowing) conditions.
- (4) Resistivity flow tests - Resistivity is determined in various flowing reactant solutions.
- (5) Redox cell performance - Performance is determined during charge and discharge at several reactant and acid concentrations and operating temperatures. Solution crossmixing and variation of resistivity with time are also monitored.

Additional information on screening methods and equipment is given in references 10 and 11.

As described in the preceding section, screening tests at Ionics, Inc., included the measurement of membrane resistivity in 0.1 N HCl. In operating cells, however, the acidity of the reactant solutions is usually 1.0 N HCl, and the reactants themselves are generally at 1.0 M concentration. The greater solution ionic strengths would be expected to result in lower membrane resistivity. But the ferric ion, especially as its concentration or that of the chloride ion is increased, tends to form negatively charged chloro complexes, which, in turn, tend to foul the membrane, increasing resistivity. For this reason the follow-up resistivity screening at Lewis is done in acidified ferric chloride solutions. Note that the resistivity tests performed at Lewis, both flow and static, expose both sides of membrane samples to the acidified ferric solutions. This is fine for screening purposes, but the measured resistivities are considerably higher than would occur in a functioning iron-chromium cell.

Although none of the development membranes produced at Ionics, Inc., during 1981 were significantly superior to the standard CD1L-AA5-LC (27.5 NP), some of the more promising ones were delivered to Lewis for further evaluation. Table 9 presents the results of flow resistivity measurements made for several concentrations of acidified ferric ion and selectivity (diffusion) measurements based on a 1-mole-per-liter concentration gradient for a 24-h interval. The membranes evaluated include those with substrates of polypropylene, polyethylene, or modacrylic. The structural variations include woven and nonwoven, a range of weave mesh, calendering, and laminates. Two resin formula variations included use of n-butanol instead of the standard isobutanol as the NP solvent.

These measurements led to the same conclusion as was reached based on Ionics' data: that none of the variations of structure or formulation provide a significant improvement over the standard CD1L-AA5-LC (27.5 NP) membrane.

TABLE 9. - SELECTIVITY AND FLOW RESISTIVITY FOR VARIATIONS IN CD1L-AA5-LC STANDARD MEMBRANE

Construction	1.0 N HCl	0.5 M Fe <sup>+3</sup> / 1.0 N HCl	1.0 M Fe <sup>+3</sup> / 1.0 N HCl	1.5 M Fe <sup>+3</sup> / 1.0 N HCl	Iron selectivity (1.0 M Fe <sup>+3</sup> , 0.5 N HCl/ 0.5 N HCl), μg Fe <sup>+3</sup> /h-cm <sup>2</sup> -M/liter	Membrane thickness, mm
	Resistivity, ohm-cm <sup>2</sup>					
Standard	3.6	3.9	5.4	10.3	21	0.43
Substrate fabric material variations						
Thin modacrylic	2.8	2.9	4.4	14.2	28	0.28
Thin modacrylic	2.6	2.6	3.9	13.8	30	.28
Melt-blown polypropylene	1.3	1.2	1.6	3.9	210	.28
Two-ply melt-blown polypropylene	2.0	---	2.6	5.0	231	.33
Melt-blown polypropylene	3.9	---	5.9	18.8	45	.71
Polyethylene mat	2.9	2.8	3.8	8.4	68	.30
Calendered mod- acrylic (n-butanol)	4.8	---	7.1	28.1	25	.48
Calendered mod- acrylic (n-butanol)	4.1	---	5.8	21.4	37	.48
Polypropylene fabric weave variations						
20x16 Scrim	3.0	2.9	4.8	12.5	38	0.76
20x16 Scrim	3.6	3.5	4.9	12.3	38	.66
10x18 Scrim	3.0	2.9	4.8	12.5	35	.76
20x20 Scrim	↓	↓	4.8	↓	22	↓
17x17 Scrim			4.8		35	
14x14 Scrim	↓	↓	4.6	↓	31	↓
14x14 Scrim	3.9	3.8	7.2	19.3	74	↓



## REACTANT COSTS

The use of chromium chloride as one of the reactants for the NASA Redox system inevitably evokes three concerns. The first has to do with assured availability, since the major suppliers of chromite ore are Zimbabwe (Rhodesia) and South Africa. This is a political question and the answer lies beyond the purview of the Redox project. The second concern has to do with the fact that chromium is a strategic material and raises the question of the impact on total world usage resulting from wide-spread application of the Redox system. According to reference 12, the amount of chromite ore required to supply one-hundred 100-MWh Redox storage plants would be equal to only about 1.6 percent of the 1976 world production. It might be added that chromium salt used in Redox systems is not chromium lost but chromium stored in a very convenient form. The final concern has to do with cost. The chromium Redox reactant is presently purchased as chromic chloride which, far from being a commodity chemical, has a very small market and is generally recovered as a byproduct of the dichromate industry. As a result, when purchased in small quantities of reagent-grade quality, it is expensive. The question then is, What would the cost be for chromic chloride if it were being produced in quantities commensurate with widespread use of the iron-chromium Redox system? To resolve this question, study contracts have been let with Allied Chemical Corp., a large producer of chromium chemicals, and Charles River Associates (CRA), a consulting firm with a strong background in hydrometallurgical processes. The object of the contracts is to derive estimates of the price of the Redox reactants (chromic chloride and ferrous chloride, both acidified with hydrochloric acid) if they were produced at a rate corresponding to one-hundred new 100-MWh storage plants per year. Such a rate is equal to about 25 000 tons of metallic chromium per year plus equivalent quantities of ferrous chloride and hydrochloric acid. The processes being evaluated start with chromite ore or ferrochrome, or the intermediate, sodium chromate. Chromite ore and ferrochrome both contain chromium and iron, and have Cr/Fe weight ratios of 1.58 and 1.64, respectively. Processes starting with sodium chromite would require that all of the requisite iron be supplied separately, probably as scrap iron. Both contractors are evaluating the direct, reductive chlorination of chromite ore. In addition, Allied Chemical Corp. is considering the chlorination of prereduced chromite ore, methanol reduction of sodium chromate, and electrolytic reduction of sodium chromate. The additional processes being evaluated by Charles River Associates are the hydrometallurgical dissolution in hydrochloric acid of chromite ore and, alternatively, ferrochrome, which is chromite ore that has been smelted with carbon and slagged off.

As a part of their cost analyses, the contractors will develop process flow sheets and mass and energy balances. Judgments will be made as to the feasibility of any new or untried processes or system components. In addition, Allied Chemical Corp. will perform sensitivity studies of the effect, on the cost of their most economical process, of variations in raw material and energy prices. Charles River Associates, in addition to the preceding analyses, will give consideration to processes for the regeneration of used Redox reactants that have undergone some prespecified degree of crossmixing through the system membranes.

TABLE 10. - SPECIFIC TOTAL REACTANT COST (1 M  $\text{FeCl}_2$ , 1 M  $\text{CrCl}_3$ , 1 N  $\text{HCl}$ ) BASED ON  
PRODUCTION RATE OF 25 000 TON/YR (22 700 METRIC TON/YR) CHROMIUM

Contractor	Production method	Cost, <sup>a</sup> \$/kWh
Allied Chemical Corp. <sup>b</sup>	Reductive chlorination of chromite ore	21.73
	Electrolytic reduction of sodium chromate	17.02
	Methanol reduction of sodium chromate	14.00
	Chlorination of prereduced ore	11.31
Charles River Associates <sup>b</sup>	Production from ferrochrome	9.20
United Technologies Corp. (baseline)	$\text{FeCl}_3$ at 19¢/lb (42¢/kg), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at 32¢/lb (70¢/kg), and $\text{HCl}$ at 29¢/lb (64¢/kg)	22.26

<sup>a</sup>Based on 80-percent utilization, 25-percent diffusional loss of capacity, and average 0.9-V discharge voltage (1.67 times the stoichiometric requirement).

<sup>b</sup>30 Percent return on investment.

TABLE 11. - TOTAL COSTS FOR PRODUCTION OF REDOX CHEMICALS (22 700 METRIC TON/YR OF CHROMIUM PLUS EQUIVALENT  $\text{FeCl}_2$  AND  $\text{HCl}$ )  
[Cost in million 1981 dollars.]

	Chlorination of prerduced chromite ore <sup>a</sup>	Methanol reduction of sodium chromate <sup>a</sup>	Electrolytic reduction of sodium chromate <sup>a</sup>	Reductive chlorination of chromite ore <sup>a</sup>	Hydrometallurgical dissolution of ferrochrome <sup>b</sup>
Total investment	<u>\$72.00</u>	<u>\$71.00</u>	<u>\$109.50</u>	<u>\$275.00</u>	<u>\$39.90</u>
Annual charges					
Raw materials	\$28.77	\$36.91	\$ 26.78	\$ 37.14	\$36.70
Energy	1.72	11.50	21.46	1.72	1.00
Labor and related costs	6.58	5.10	6.58	6.58	1.60
Fixed capital charges	10.10	10.80	17.10	40.00	4.70
Administrative expense	2.80	2.70	2.70	3.00	2.10
Return on investment, 30 percent	<u>21.60</u>	<u>21.50</u>	<u>32.90</u>	<u>82.50</u>	<u>11.97</u>
Total annual charges	\$71.57	\$88.51	\$107.52	<sup>c</sup> \$137.64	\$58.07
Total reactant cost per kg $\text{CrCl}_3$	\$ 1.04	\$ 1.28	\$ 1.55	\$ 1.99	\$ 0.84

<sup>a</sup>Study by Allied Chemical Corp.

<sup>b</sup>Study by Charles River Associates.

<sup>c</sup>Includes credit for sale of  $\text{MgCl}_2$  and  $\text{AlCl}_3$ , \$33 300 000.

TABLE 12. - SPECIFIC TOTAL SYSTEM FACTORY COST BASED ON  
PRODUCTION OF ONE-HUNDRED 10-MW/100-MWh  
SYSTEMS PER YEAR

	System factory cost, \$/kWh
As developed by United Technologies Corp.: 2 M reactants at \$22.26/kWh; tankage at \$0.60/gal (\$0.158/liter)	62.27
As modified to reflect lower reactant and tankage costs (Allied Chemical Corp.): 1.5 M reactants at \$11.31/kWh, tankage at \$0.24/gal (\$0.063/liter)	44.80

A summary of the estimated total cost of reactants ( $\text{CrCl}_3$ ,  $\text{FeCl}_2$ , and  $\text{HCl}$ ) for the processes evaluated during 1981 are presented in table 10. Included in the table is the reactant cost that was given by NASA Lewis to United Technologies Corp. for use in a study of the production cost of complete Redox systems (ref. 13). This value, \$22.26/kWh, was assumed to be a very optimistic projection. However, as seen in the table, it is about the same as the most expensive process evaluated to date, and 42 percent greater than the least expensive.

Capital costs and annual charges are presented for each of the presently completed processes in table 11. The return on capital investment is assumed to be 30 percent. It can be seen that Allied's reductive chlorination process, which involves the most uncertain technology of the processes evaluated, is very capital intensive. On the other hand, the hydrometallurgical processing of ferrochrome, analyzed by CRA, has a high cost for the feed material but is a simple, straightforward process and therefore relatively inexpensive.

Reactant costs are a significant portion of total system costs. Thus these reductions in projected costs are very encouraging with respect to the economic viability of Redox systems. Table 12 shows the impact on the total system cost developed by UTC when the original reactant cost assumption is replaced by Allied's projection for the process of chlorination of prereduced ore. Included in the revised estimate is a reduction in tankage cost to reflect a standard chemical industry approach to storing bulk quantities of corrosive fluids.

#### CONCLUDING REMARKS

The results of the Redox Project effort during calendar year 1981 were encouraging. A very significant accomplishment was the development of an understanding of the behavior of the chromium reactant during the charging process. The determination that two complexed species of the chromic ion predominate at room temperature, and that only one is electrochemically active, explained anomalous characteristics of Redox cells. Subsequently it has been shown that operation at higher temperatures favors the active species and greatly improves cell performance with respect to these characteristics.

Cost analyses being performed under contract indicate that the reactants for the iron-chromium Redox system can be provided at a surprisingly low cost when produced in large quantities. If the reactants truly are inexpensive enough, the door is opened for the mixed-reactant concept, in which each reactant solution in the uncharged state contains both ferrous chloride and chromic chloride. This concept offers several very attractive characteristics that may counterbalance the increased reactant cost.

During 1981, there were no significant advances in either the electrode or membrane technologies. However, in the light of the new requirement for operation at higher temperatures, both of these development areas will have to be refocused and may enter into entirely new, and perhaps more fruitful, avenues of inquiry.

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16. Abstract The most significant development in the NASA Redox Storage System Development project during calendar year 1981 was the demonstration that raising the operating temperature from 25 <sup>0</sup> C to 65 <sup>0</sup> C greatly enhances the kinetics of the chromium electrode charging reactions. The design of the auxiliary electrochemical cell, which is used to keep both reactants at the same state of charge, was modified, leading to better and more stable performance. Preliminary testing has shown that the four-tank mode of operation improves energy efficiency as much as 5 percentage points over the conventional two-tank mode. Another variation in operating mode, the use of mixed reactants, potentially offers several very attractive advantages. Preliminary reactant cost studies lend further weight to the feasibility of the mixed-reactant concept. Electrode studies have shown that reproducibility of performance is very dependent on the pyrolysis temperature at which the carbon/graphite felt substrate is formed. Membrane development work continued to concentrate on cost reduction and the enhancement of resistivity and selectivity. The project effort was supported by the Division of Energy Storage Systems of the Office of Conservation and Renewable Energy of the U.S. Department of Energy under Interagency Agreement DE-AI04-80AL12726. Project supervision was provided by the Storage Batteries Division of Sandia National Laboratories.					
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