DOE/NASA/12726-23
NASA TM-83469

NASA Redox Storage System Development Project

Calendar Year 1982

National Aeronautics and Space Administration
Lewis Research Center

October 1983

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

DISCLAIMER

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
NTIS price codes[1]
Printed copy: A03
Microfiche copy: A01

---

[1] Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication, NTIS-PR-360 available from NTIS at the above address.

DOE/NASA/12726-23
NASA TM-83469

DOE/NASA/12726--23

DE84 002196

NASA Redox Storage System Development Project

Calendar Year 1982

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

October 1983

Work performed for
U.S. DEPARTMENT OF ENERGY
Conservation and Renewable Energy
Division of Energy Storage Systems
Washington, D.C. 20545
Under Interagency Agreement DE–AI04–80AL12726

NASA REDOX STORAGE SYSTEM DEVELOPMENT PROJECT

Calendar Year 1982

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

SUMMARY

The calendar year 1982 effort grew from the discovery during the previous year that the iron/chromium Redox system must operate in the temperature range 55° to 65° C in order to avoid kinetic difficulties with the chromium redox reaction. Membrane and electrode studies which were then underway at 25° C, being performed by Ionics, Inc., and Giner, Inc., respectively, have been completed, and the results became the starting points for proceeding to elevated-temperature operation. At NASA Lewis single-cell evaluation of the mixed-reactant mode of operation at elevated temperature has lead to significant advances in cell power density and in energy efficiency.

The effort of Ionics, Inc., to develop Redox cell membranes focused for most of the year on ways to reduce resistivity. Several approaches were taken. The first was merely to incorporate thinner substrates than the usual calendered woven modacrylic. Generally, successful resistivity reductions by this approach were accompanied by an unacceptable worsening of selectivity. The other path taken was to develop heterogeneous, two-layer structures consisting of a sturdy, fabric-supported, low-resistivity, polymer "board" bonded to a thin film of highly selective ion exchange material to provide selectivity. Various polymer chemistries were used for both layers. Even the best of these structures was only marginally superior to the standard CD1L.

Analytical studies were carried out at NASA Lewis on the sensitivity of projected system cost and efficiency to membrane resistivity and current density. These studies indicated that current densities in the range 50 to 75 mA/cm^2 are required to keep stack costs reasonable. However, to obtain acceptable energy efficiencies at such current densities, membrane resistivities at least as low as 1.5 ohm-cm^2 are required. The 2.6-ohm-cm^2 resistivity of the standard CD1L membrane at 25° C was unsatisfactory with regard to resistivity.

Analytical studies of the relationship between system maintenance requirements and membrane selectivity showed that the optimum CD1L membrane, with a room temperature selectivity of about 20 $\mu\text{g Fe/h-cm}^2\text{-M}$, was also marginal with regard to reactant refurbishment requirements. To prevent cross-mixing from proceeeding beyond some moderate amount, say 10 percent, batch treatment of the reactants would be required at intervals so frequent as to be too costly. Thus, the present best membrane for 25° C operation with separate reactants appeared to be marginal with respect to both resistivity and selectivity, and modifications to improve either property seemed always to be detrimental to the other. On top of this, selectivity measurements at Lewis on developmental membranes from Ionics, Inc., and other sources showed that raising the temperature to 65° C, while reducing resistivities by a factor of 2 or 3, resulted in up to a tenfold worsening of selectivities.

These studies and associated experimental work combined to show, with the

present generation of membranes at least, that controlling cross-diffusion of the reactants while operating efficiently at or near 65° C was not feasible. No option was left but to determine whether acceptable cell performance could be achieved at 65° C using reactants that were totally mixed from the start. The results attained in this mixed-reactant, elevated-temperature mode of operation were very encouraging. The first cell tested contained the standard gold-lead catalyzed chromium electrode and a developmental cation membrane (known to be very "open") with a low resistivity. Both reactant solutions in the fully discharged state were identical. The results were promising, with the cell achieving high current density (64.5 mA/cm^2), essentially complete utilization of the reactants, low hydrogen evolution rate, and high energy efficiency. A singular advantage to operating with mixed reactants is that if any partitioning of reactants or any osmotic transfer of solvent should occur across the membrane, it can be countered simply by discharging the cell, reblending the reactant solutions, and then redistributing them. The only penalties associated with the mixed-reactant mode of operation at elevated temperature are a loss of about 50 to 70 mV in open-circuit voltage, a decrease in coulombic efficiency, and an increase in reactant cost. This cost increase for reactants is balanced against a reduction in stack cost because of the ability to operate at high current densities and a further reduction due to the use of much less expensive membranes. Also, with regard to reactant cost, it has been shown by studies completed during the year that these costs should not preclude operation with mixed reactants.

At Lewis studies were carried out to understand why some chromium electrodes, after being cycled in working cells for some months, start to evolve hydrogen at increasing rates. Of particular concern, in light of the switch to mixed-reactant operation, was the possibility that reactant cross-mixing per se was the culprit. Tests of this hypothesis indicated that exposure of the gold-lead catalyzed chromium electrode to iron in the ferric (+3) oxidation state could, indeed, lead to increased hydrogren evolution. However, the occurrence of the ferric ion in the chromium reactant system requires a relatively unusual sequence of events to occur, and this sequence is easily avoided. Iron in the ferrous (+2) state was shown to have no detrimental effect on chromium electrode performance.

Another cause of the hydrogen evolution was the contamination of the reactant system with trace amounts of platinum from the hydrogen electrode of the rebalance cells typically used in conjunction with working cells. Apparently, the platinum was dissolving and migrating first into the iron stream and ultimately into the chromium reactant system, where it was reduced to the metal. Significantly, these causes of increased hydrogen evolution were related to operational occurrences that can be easily avoided in practice.

Other electrode work carried on at Lewis involved the in-cell evaluation of alterntive chromium electrode catalysts for elevated temperature operation. These catalysts included a planar structure given enhanced surface area by ion-etching, lead (alone), silver-lead, and bismuth-lead. The ion-etched electrode, even with lead added, was too active in the evolution of hydrogen. Charging proceeded well with lead as the catalyst on the standard carbon felt substrates, but the discharge was irreversible. The silver-lead combination performed poorly for both charge and discharge. However, the bismuth-lead catalyst showed excellent properties. At 65° C it is active for the chromium redox reactions; it is reversible and stable; and it has a high hydrogen overpotential. This catalyst also has given evidence of being far more "forgiving" than the standard gold-lead formulation when anomalies do occur.

The bulk of the recent electrode work at Giner, Inc., involved the gold-lead catalyst combination at 25° C, evaluated by cyclic voltammetry. One part of the effort was to evaluate various changes in the standard method of cleaning and applying gold to felt substrates. In general, these changes did not result in the production of electrodes with better performance. By using electron microscopy, it was ascertained that performance improved as gold particle size decreased; but a correlation could not be made between the method of catalysis and the resultant gold particle size.

With regard to operation with mixed reactants, Giner, Inc., found that adding ferrous chloride to the chromium reactant enhanced electrode performance, while the addition of chromic chloride to the iron reactant inhibited it. Because of the low reactant concentrations used, however, the significance of these results with regard to actual Redox cell operation is not yet known.

The result of the 1982 Redox technology development effort has been to increase the level of confidence in the viability of the iron-chromium system concept. Although testing has not yet been extensive, initial results indicate that operation with mixed reactants at elevated temperatures has many advantages and may be the breakthrough needed for the Redox system to fulfill its early promise as an economical, long life storage device.

INTRODUCTION

During calendar year 1982, the focus of the Lewis Redox Project was on technology issues. Very little was done in the systems areas such as scale-up, applications analysis, component development, etc. Instead, most of the effort involved single-cell experimentation, with the goal of building on the technical developments and advances of the previous several years. During those years, many of the difficulties being encountered during operation of iron-chromium Redox cells were shown to be directly related to the chemistry of the chromic ion reactions (ref. 1). The chromic ion (Cr^{+3}), which is the discharged form of the chromium reactant, exists as two distinct species, only one of which is electrochemically active. The equilibrium concentrations of these species at room temperature are about equal, and the rate of equilibrium is slow. These characteristics caused the operational problems with the iron-chromium Redox cells. Fortunately, it was later shown that raising the chromium reactant temperature to 55° to 65° C shifts and accelerates the equilibrium to favor the electrochemically active chromic ion species. This permits charging at higher rates with lower applied voltages and the full utilization of the reactant theoretical capacity. It was with these new understandings that the 1982 work was begun. The aim was to exploit the technological logic as it unfolded under the imperative of elevated temperature operation.

ELECTRODE DEVELOPMENT

NASA Lewis

Because it is necessary to catalyze the chromium electrode, the question of catalyst poisoning or degradation due to the presence of iron cations in the chromium reactant solution was of concern. As will be discussed in detail in following sections, to date no membrane has been developed that has a suitably low resistance yet is able to perfectly separate the respective reactant metal cations. Initial evaluation of this potential problem involved the incremental addition of ferrous chloride to the chromium solution of a working cell and measuring the rate of hydrogen evolution at the gold-lead catalyzed chromium electrode during normal cycling. As the $FeCl_2$ concentration in the chromium reactant was increased from 1 to 40 percent of the chromium salt concentration, the rate of hydrogen evolution increased commensurately. This conflicted with cyclic voltammetry studies being carried out under the contract with Giner, Inc., which showed virtually no effect of $FeCl_2$ additions to the chromium reactant solution. Therefore, the test was repeated with fresh reactants and unused cell components, but this time the ferrous chloride solution was rebalanced (ref. 2) before addition to the chromium solution to assure that no ferric ion was present. (Rebalancing involves the use of an electrochemical cell to reduce ferric ion (Fe^{+3}) to the ferrous ion, using hydrogen as the reducing agent.) Over the next 3 months, the cell was continuously cycled to increasingly deeper depths of discharge (from 80 percent to 95 percent DOD) with 40 percent $FeCl_2$ in the chromium reactant. During this time the change in the hydrogen evolution rate was from 1 to about 3 percent of charge capacity. At the end of this 3-month period, the cell was allowed to get out of balance and then to sit short-circuited while fully discharged. This in effect created an iron-iron concentration cell which caused the generation of ferric ions (Fe^{+3}) in the chromium reactant. On subsequent cycling, the hydrogen evolution rate from the chromium electrode was about four times greater than before, being about 12 percent of charge capacity. Attempts to restore it to previous performance were unsuccessful. Thus, it was the ferric ion that attacked the gold-lead catalyst of the chromium electrode, causing an irreversible change that somehow negated the high hydrogen overpotential of the lead component of the catalyst. All of this agrees with the earlier observation that the exposure of a fully catalyzed, used chromium electrode to air results in greatly increased hydrogen evolution when the electrode is reused in a cell. This seems to indicate that exposure of a catalyzed chromium electrode to an oxidizing environment can bring about undesirable and irreversible changes.

These results were quite encouraging because they indicated that the previously noted tendency for long-term increases in the hydrogen evolution rate were not associated with the electrode per se or with any aspect of the iron-chromium Redox cell concept. Rather, the problem is an operational difficulty which results from allowing a rather specialized sequence of events to occur. This sequence, once recognized, is easily avoided.

All the above results and observations were corroborated in other cells; and operational procedures were established to prevent oxidation of the chromium electrode catalyst. Nonetheless, subsequent instances of increasing gas evolution from a working cell occurred. Finally, the components of a cell that had failed in this mode were analyzed by X-ray techniques. Surprisingly, platinum was discovered in the membrane taken from the cell. Platinum is a splendid catalyst for the reduction of water by chromous ions, thus generating hydrogen. Ironically, the source of the platinum was the hydrogen electrode of the rebalance cell, the purpose of which was to consume any evolved hydrogen. A sketch of a rebalance cell is presented in figure 1. Typically, a short-circuited rebalance cell was used with each working cell on test, to keep the reactants chemically balanced. This was accomplished by using the evolved hydrogen, which was collected in the chromium reservoir (or with hydrogen supplied from an external source), to electrochemically reduce the excess ferric ions. The iron reactant solution exiting the working cell, therefore, flowed through the rebalance cell before returning to the iron reservoir. Apparently, the platinum catalyst on the hydrogen electrode of the rebalance cell was going into solution, diffusing through the rebalance cell membrane into the flowing iron stream, and then migrating through the working cell system until encountering chromous ions in, or at the surface of, the working cell membrane. Here, the platinum ions were reduced to the metal which then began to catalyze the chemical reaction between chromous ion and water to yield hydrogen.

Later analyses of components of other cells that have undergone increased hydrogen evolution rates while being tested in conjunction with rebalance cells have also shown the presence of platinum in the membranes. Again, as was the case with the indication that exposure to the Fe^{+3} ion could cause increased hydrogen evolution, this is a satisfying result: It shows that another major cause of increased hydrogen evolution is merely operational and not inherent to the gold-lead catalyst or the system concept.

Of course, since there will always be some small rate of hydrogen evolution due to electrochemical reduction during the charging process, plus other causes of system imbalance, the use of a rebalance cell will remain necessary. Therefore, a means to avoid or alleviate the platinum contamination problem must be developed. Several possible approaches, each promising, will be evaluated in 1983. In the meantime gas traps now are being used to collect and measure any hydrogen produced from working cells on test.

During 1982 a variety of alternative catalyst approaches for the chromium electrodes were examined. Studies were carried out both at room temperature and at 65° C, as the project began to shift its emphasis toward elevated-temperature operation. These studies were carried out according to the conventional concept of keeping the reactants separated by a highly selective membrane and also according to the new, mixed-reactant concept of operation. This latter concept will be discussed in some detail in later sections of this report. In the mixed reactant mode of operation both reactant solutions, when fully discharged, are identical. Typically, the composition would be 1.0 M $FeCl_2$, 1.0 M $CrCl_3$, and 2.0 N HCl.

Concerning the chromium electrode catalysis, the first question addressed was whether, at elevated temperature, any gold catalyst was indeed required. It was hoped that at 65° C the carbon felt electrode substrate would have sufficient intrinsic electrochemical activity for the chromium Redox reactions. Therefore, a cell was assembled with a bare carbon felt chromium electrode and cycled at 65° C. Unmixed reactants were used, and the standard quantity of saturated $PbCl_2$ solution was added to the chromium solution so that during charging a thin lead deposit would lessen the tendency toward hydrogen evolution. The cell did charge with very low hydrogen generation. However, polarization curves at 50 percent state-of-charge (SOC) (fig. 2) revealed irreversible behavior for both charge and discharge.

Next, a cell with the standard gold-lead catalyst was cycled intermittently for a total of 104 cycles at temperatures to 65° C, with unmixed reactants, to evaluate the effect of elevated temperature on this catalyst composition. Although the resistivity of the RAI Research Corporation developmental membrane had increased significantly, polarization curves at the end of the

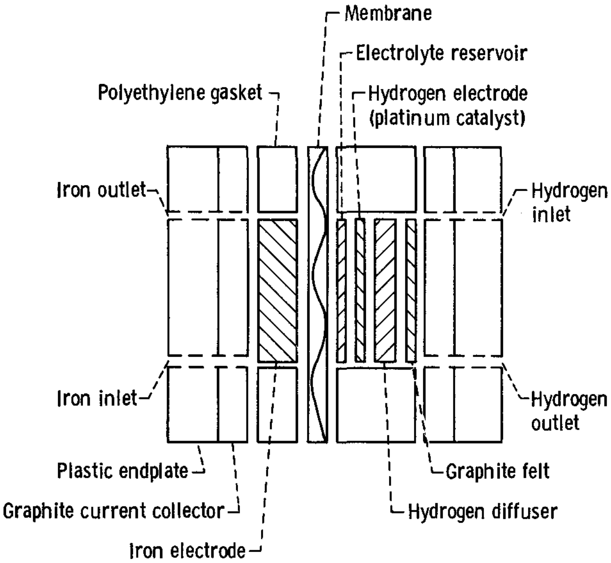

Figure 1. - Ferric chloride-hydrogen rebalance cell schematic.

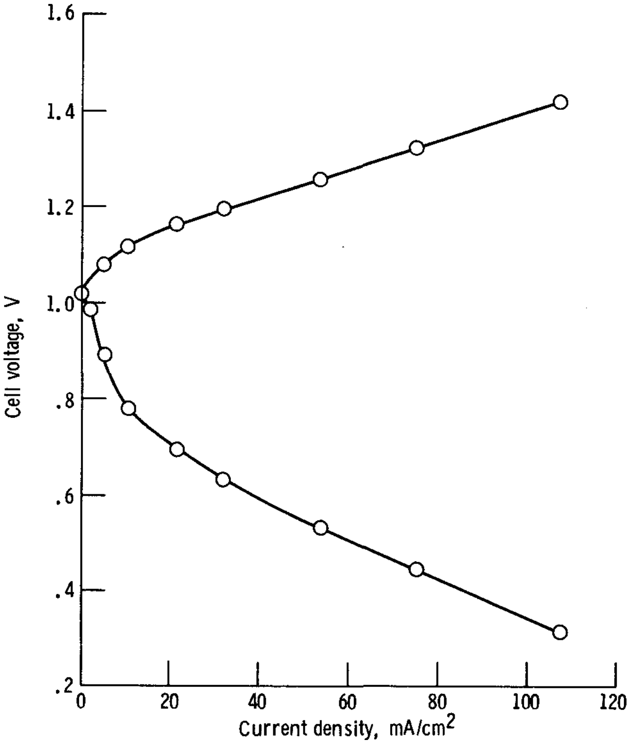

Figure 2. - Charge and discharge polarization curves for cell with lead-catalyzed chromium electrode. Temperature, 65° C; unmixed reactants; 50 percent SOC.

test period showed that electrode performance remained reversible (fig. 3). However, hydrogen evolution during operation at 65° C was consistently in the neighborhood of 6 percent of charge capacity, compared with 1 to 3 percent at room temperature. Generally, for all cells operated at 65° C, with the gold-lead catalyst, the higher temperature did not cause any deterioration in polarization performance or gassing rate during the respective test periods. However, the actual magnitude of the hydrogen evolution rate did vary from cell to cell, ranging from less than 1 percent to the aforesaid 6 percent. In a large enough system generating significant quantities of hydrogen, the rebalance stack(s), instead of simply being short-circuited, could be used as a power source for small loads such as pumps. In this situation the evolution of hydrogen would not be a net coulombic loss mechanism. Even in the absence of this advantage, it is possible that a gassing rate of 6 percent would be acceptable in specific applications. Nonetheless, it was obviously worthwhile to explore other possible chromium electrode catalyst systems.

Another attempt was made to take advantage of the elevated operating temperature so that catalysis of the chromium electrode would not be required. A planar carbon surface was ion-etched to greatly increase its surface area. Tested as a chromium electrode in a working cell at room temperature, the ion-etched plate, unfortunately, showed far more activity for hydrogen evolution than for the chromium Redox reactions. Heated to 55° C, the performance was even worse. The addition of bismuth and lead salts to the chromium reactant solution in order to depress hydrogen evolution was beneficial, but the net improvement left much to be desired (fig. 4). Probably, the attempt to deposit a material such as lead on this surface structure resulted in an uneven distribution, with high spots being plated while recessed regions were not. Also, the "fuzzy" character of the ion-etched surface undoubtedly leads to the growth of an appreciable mass-transport boundary layer which inhibits performance.

An analog of the gold-lead catalyst, using silver instead of the gold, was next evaluated. The rationale for this selection was that silver, having a lower reduction potential than gold would be more easily stripped and redeposited, making possible a restoration of performance after deterioration, as evidenced by increasing hydrogen evolution rates. At 65° C with mixed reactants, the initial hydrogen rate from a cell using this chromium electrode catalyst was low. However, the electrode was irreversible for the chromium redox reactions and showed several steps in the current-voltage curves during constant load discharges.

The final chromium electrode catalyst system evaluated in 1982 was bismuth-lead. The rationale for this selection was pretty much the same as for the silver-lead system. The choice was supported by evidence from cyclic voltammetry evaluations carried out at Giner, Inc., that bismuth was active for the chromium redox reactions (ref. 3). This metal also is known for its hydrogen reduction overpotential. The brief period of testing of this catalyst system at the end of 1982 gave extremely encouraging results (ref. 4). Used in a working cell at 65° C with mixed reactants, hydrogen evolution was very low, electrode performance was reversible, and cycling between 95 and 0 percent SOC revealed no catalyst instability. Cell voltage versus time (equivalent to SOC) for a charge-discharge cycle at 64.6 mA/cm^2 is shown in figure 5. Results of a similar test with a cell using the standard gold-lead chromium electrode catalyst are shown in figure 6 for comparison. There is much to be said about these two tests, and they will be discussed further in the later section concerning the mixed-reactant concept. For now, the significant point is that the

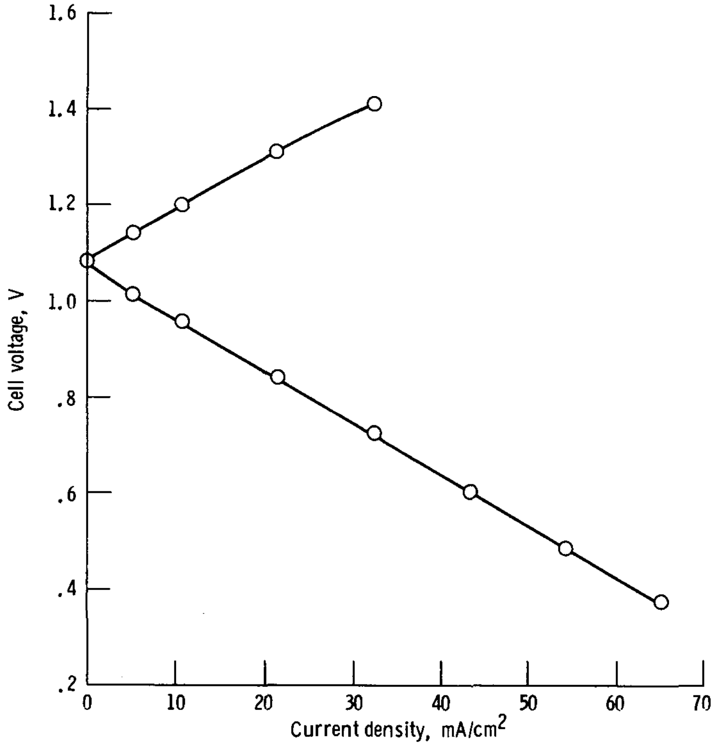

Figure 3. - Charge and discharge polarization curves after 104 cycles for cell with standard gold-lead catalyst for chromium electrode. Temperature, 65° C; unmixed reactants; 50 percent SOC.

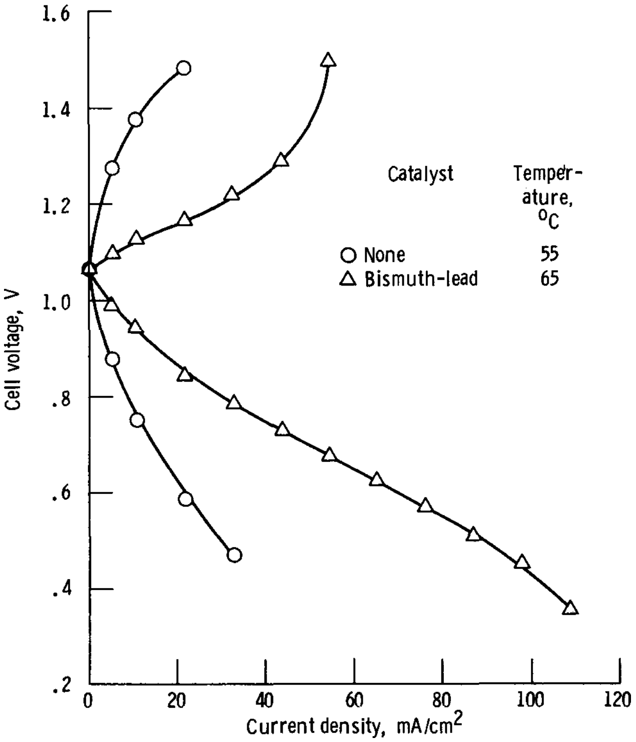

Figure 4. - Charge and discharge polarization curves for a cell with an ion-etched carbon plate for the chromium electrode. Unmixed reactants; 50 percent SOC.

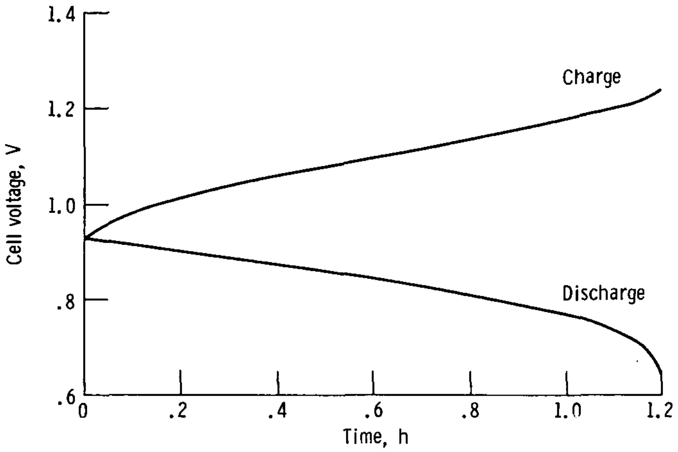

Figure 5. - Cell voltage during a constant-current cycle. Current density, 64.5 mA/cm^2; temperature 65° C; mixed reactants; bismuth-lead chromium electrode catalyst; 0 to 87 percent SOC. Cell resistivity, 1.74 Ω-cm^2; membrane resistivity, 0.34 Ω-cm^2; energy efficiency, 73.1 percent; coulombic efficiency, 94.6 percent; voltage efficiency, 77.2 percent; hydrogen evolution, 0.2 percent of charge capacity.

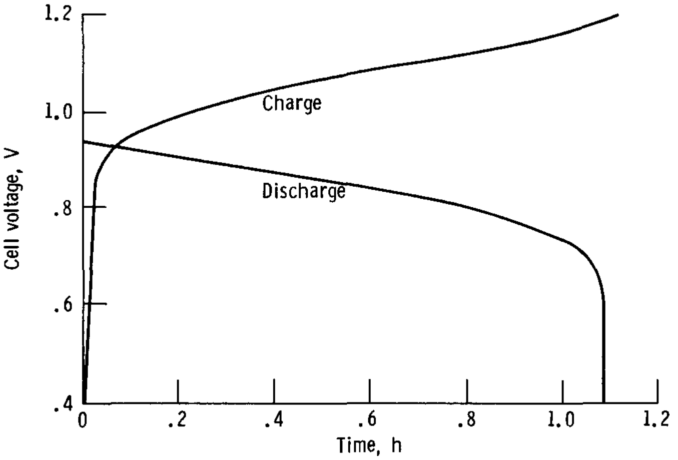

Figure 6. - Cell voltage during a constant-current cycle. Current density, 64.5 mA/cm^2; temperature, 65° C; mixed reactants; gold-lead chromium electrode catalyst; 0 to 87 percent SOC. Cell resistivity, 1.76 Ω-cm^2; membrane resisitvity, 0.36 Ω-cm^2; energy efficiency, 72.3 percent; coulombic efficiency, 92.2 percent; voltage efficiency, 78.4 percent; hydrogen evolution, 0.9 percent of charge capacity.

bismuth-lead electrode catalyst showed electrochemical activity for the chromium redox reactions that was fully the equal of the gold-lead catalyst. Furthermore, the tendency for hydrogen evolution was very low.

The in-house electrode development effort of 1982 produced the very encouraging evidence that a chromium electrode catalyst has been produced which meets requirements for elevated temperature operation. It is electrochemically active, stable, and reversible and has a high hydrogen overvoltage. Furthermore, the bismuth component is more easily applied than the gold component of the previous standard catalyst.

Giner, Inc.

During calendar year 1982, under contract DEN3-262, Giner, Inc., has focussed on the gold-lead catalyzed chromium electrode for operation at room temperature (25° C). One goal of this effort was to develop the techniques necessary to consistently produce catalyzed electrodes with suitable electrochemical performance. The analytical tool used in most instances was cyclic voltammetry The elements of the electrode production sequence that were examined included the formation of the felt substrate from its precursor (ref. 5) and the subsequent cleaning and gold catalyzation of the felt. The second aspect of the contract effort was to evaluate the effect of certain operational characteristics on electrode performance, again by cyclic voltammetry. The characteristics studied were the cross-mixing of the reactants and the acidity level of the chromium reactant solution. The study of the effect of elevated temperature is also a part of the contract effort but was not begun during 1982. In all these tasks the performance measurements were carried out at room temperature, even though it seems quite certain that actual Redox system operation will be in the 55° to 65° C range. This was a matter of convenience coupled with the belief that the conclusions reached based on room temperature experiments would not be significantly different had the experiments been performed at some other temperature.

The first task of the contract effort was to systematically evaluate the effect on ultimate electrode performance of the temperature at which the Rayon felt precursor was pyrolyzed to carbon or graphite. A series of felt samples was prepared by Fiber Materials, Inc., at processing temperatures of 1250°, 1350°, 1500°, 1650°, 1800°, and 2300° C, and delivered to Giner, Inc. The samples were cleaned in potassium hydroxide and catalyzed with a gold loading of 12.5 $\mu g/cm^2$ according to a standardized procedure (ref. 6). Cyclic voltammetry was then used to evaluate the electrode samples in terms of hydrogen evolution and chromium activity. Analysis for hydrogen evolution indicated decreasing hydrogen ion reduction with increasing felt processing temperature (fig. 7).

In general, little change in hydrogen evolution occurs beyond a processing temperature of 1800° C. The chromium redox reaction activity of the six felt samples decreased with increasing processing temperature. Probably the most relevant overall measure of relative electrochemical efficiency is the comparison of chromium redox activity and hydrogen evolution. The ratio of the quantity of chromous ion oxidized to the quantity of hydrogen ion reduced per voltammetry cycle for each process-temperature sample of felt is shown in figure 8. The 1650° and 1800° C felts are the most favorable on this basis.

Two alternative catalysis techniques for the deposition of gold on the felt electrode samples were compared with the standard technique used at Lewis. One technique simply used a larger volume of a more dilute alcoholic gold chloride solution for soaking the felt. The second approach involved two separate soaks and extra furnace drying steps. Results obtained by cyclic voltammetry for samples catalyzed by these three methods were compared. Hydrogen evolution on the electrodes prepared according to the Lewis standard technique was lower than for either of the other methods. The ratio of chromium redox activity to hydrogen reduction was also better for the standard technique.

Electron microscopy was used to determine gold particle size on the electrodes prepared by the three catalysis approaches (ref. 5). Cyclic voltammetry was then used to see if there was a correlation between the gold distribution and the electrochemcal performance of the electrodes. Felt samples having smaller gold particle sizes exhibited high chromium activity and high hydrogen evolution rates. Indications are that the gold deposition process may occur by adsorption from a colloidal state induced by contact of the gold solution with the carbon felt. In general, the Lewis standard catalysis method gave the best electrochemical performance, which seems to correspond to an intermediate gold particle size.

Although variations in results were observed, the two lowest process-temperature felts (1250° and 1350° C) are consistently less suitable for the chrominum electrode application. Thus, the carbon felt substrate still seems to be a contributor to variabiliy in results by influencing the gold deposition process.

The effect of ferrous chloride ($FeCl_2$) on the electrochemical performance of a gold-catalyzed electrode in a chromic ion solution was determined. The $FeCl_2$ concentration of the chromium solution was incrementally increased from 0 to 0.5 molar. The results (fig. 9) show that the chromic ion reduction reaction was shifted to slightly more negative potentials and that the total quantity of chromium reacted increased as the $FeCl_2$ concentration increased. In addition, hydrogen evolution decreased with increasing $FeCl_2$ concentration. Thus, it seems that the presence of $FeCl_2$ in the chromium reactant solution has a beneficial effect, perhaps due to a shifting of the chromic ion equilibrium to favor the electrochemically active monochloropentaaquo species.

The effect of chromic chloride ($CrCl_3$) on the iron redox reactions was observed in a similar way. (See fig. 10.) The incremental additions of $CrCl_3$ increasingly depressed the level of the iron redox reactions. From these unexpected results it is apparent that the presence of $CrCl_3$ interferes with the iron redox reactions, perhaps by increasing the chloride complexes of the ferric ion.

MEMBRANE DEVELOPMENT

Ionics, Inc.

The 1982 contract effort at Ionics, Inc., was established before the decision by Lewis to concentrate on cell operation at a temperature of 65° C. The 1982 work was, therefore, an extension of the previous contract effort (ref. 7) and focused primarily on improving membrane resistivity at 25° C.

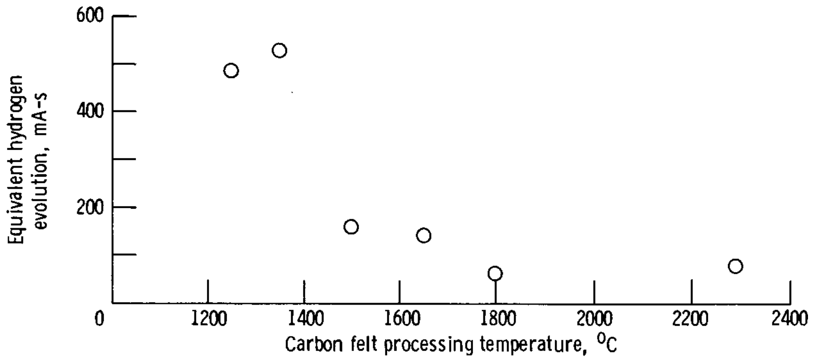

Figure 7. - Effect of processing temperature on subsequent hydrogen evolution from a gold-lead-catalyzed, carbon-felt electrode (evaluated by cyclic voltammetry).

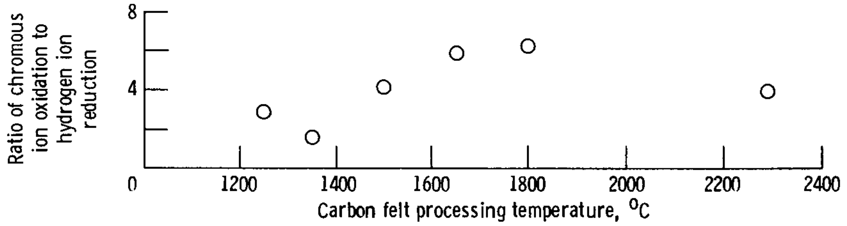

Figure 8. - Effect of processing temperature on subsequent activity for chromous-ion oxidation and hydrogen-ion reduction by a gold-lead-catalyzed, carbon-felt electrode (evaluated by cyclic voltammetry).

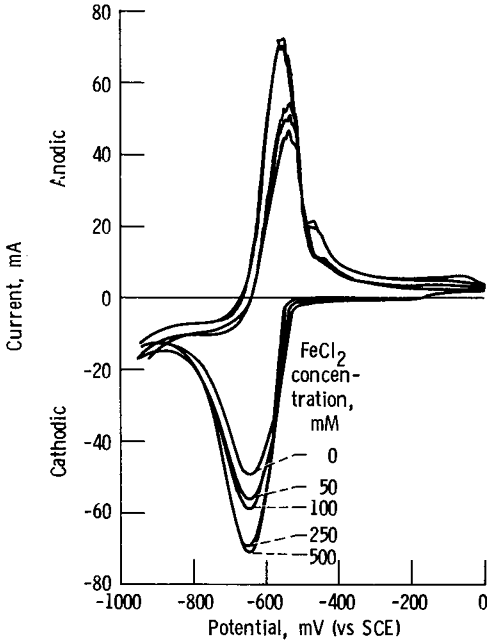

Figure 9. - Effect of $FeCl_2$ additions on chromium redox reactions. Gold-lead catalyst; $[CrCl_3] = 50$ mM.

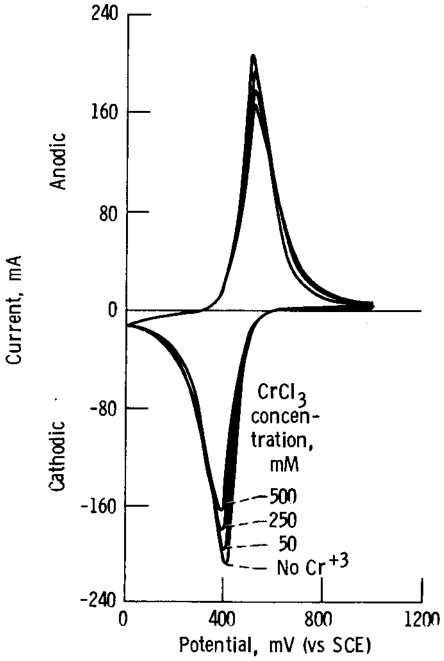

Figure 10. - Effect of $CrCl_3$ additions on iron redox reactions. $[FeCl_2] = 50$ mM.

Several approaches were evaluated for the reduction of membrane resistivity. The one that received major emphasis involved heterogeneous structures consisting of two bonded layers: one a highly porous, fabric-supported low-resistance "board" to provide strength and the other a much thinner, tighter, and more highly charged film to provide selectivity. The boards were given a porous character by a nonpolymerizable (NP) content ranging from 50 to 70 percent in the resin composition. The resin used in these boards contained chloride, amine, or oxirane functional groups to provide compatibility with films of various chemistries. The resistivities of the boards and the various board-film composites were measured in 0.1 HCl in the standard way. Although some of the composites had resistivities as low as 3.4 ohm-cm^2, there was not a great improvement over the standard CD1L value of about 4.1 ohm-cm^2.

Another approach toward resistivity reduction that was evaluated was the use of thinner membrane substrate, including materials other than the standard calendered woven modacrylic. Table I presents for these membranes resistivities measured by Ionics, Inc., and 24° and 55° C selectivities measured at Lewis. Some of these membranes will be evaluated at Lewis in working cells operating at 65° C.

Toward the end of 1982, Ionics, Inc., began to develop and deliver to Lewis anionic and cationic membranes for in-cell evaluation at elevated temperature in the mixed reactant mode of operation, which will be discussed in a later section. Ionics, Inc., has also initiated stability tests on likely membrane candidates, soaking them 1000 h at 65° C in 1 M $FeCl_3$ acidified to 1 N with HCl.

NASA Lewis

By the beginning of 1982 no ion exchange membrane had been developed that offered a really attractive combination of low resistivity and good selectivity - the ability to prevent cross-diffusion of the reactant metal cations. The difficulty, of course, is that these two properties are opposed to one another. Anything done to decrease resistivity, for example, tends to cause a deterioration in selectivity. Therefore, the best combination of properties that was arrived at represented a compromise between conflicting ideals. Furthermore, all the indications were, at least for the present generation of membranes, that the learning curve had gone flat. That is to say that only marginal improvements were being made in either of the characteristics, and these improvements were always accompanied by unacceptable changes in the other characteristics.

To get a better measure of the existing situation, a set of sensitivity studies was carried out. The effects of membrane resistivity on calculated system efficiency and cost, with current density as a parameter, were determined first. The results are presented in figures 11 and 12. The range of resistivities (1.5 to 2.25 ohm-cm^2) is considered in the light of the existing best value of 2.6 ohm-cm^2, which results from a trade-off between membrane resistivity and selectivity. For low current densities, efficiency is not very sensitive to changes in resistivity. However, the penalty in system cost for operating at these low current densities is significant. (These system cost projections include the factory cost for hardware and the sales price for reactants, both of which are based on assumed mass production.) One conclusion to be derived from these results is that from a cost standpoint, current densities

TABLE I.- RESISTIVITIES AND SELECTIVITIES AT 24° and 55° C, FOR IONICS, INC., MEMBRANES WITH CD1L RESIN ON VARIOUS SUBSTRATES

Substrate	Thickness, cm	Nonpolymerizable content, percent	Resistivity in 0.1 N CHl, ohm-cm^2	Selectivity, µg Fe/h-cm^2-M	Temperature, °C
Woven modacrylic	0.041	30	4.1	24	24
		35	3.7	60	24
		40	3.7	107	24
				201	55
Fine woven modacrylic	0.038	30	3.9	19	24
		35	3.7	65	24
		40	3.6	148	24
		40		224	55
Nonwoven modacrylic	0.32	30	2.7	59	24
		30		139	55
Golden Aramid (on Kevlar)	0.013	30	3.2	31	24
		30		91	55
		35	3.4	81	24
		35		159	55
		40	3.4	129	25
		40		221	55
CD1L-AA5-LC (standard)	0.052	27.5	4.2	20	24
		27.5		95	55

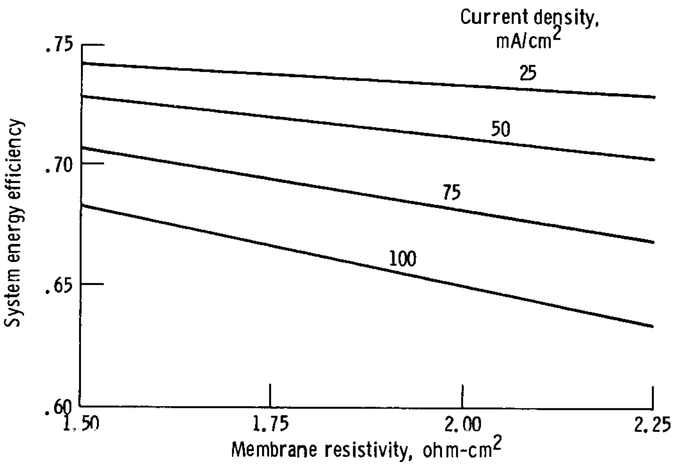

Figure 11. - Effect of membrane resistivity on Redox system energy efficiency.

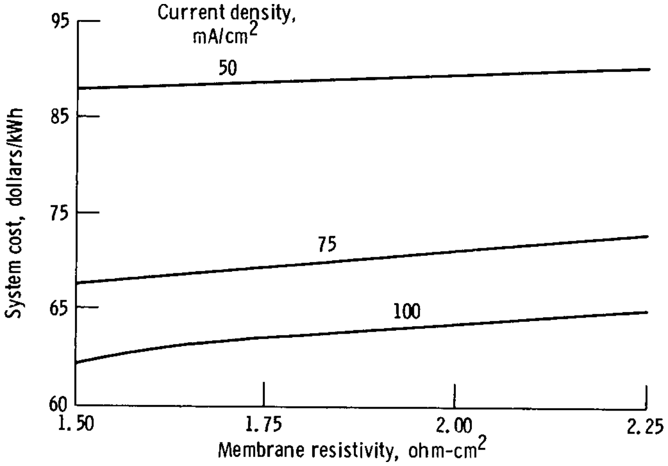

Figure 12. - Effect of membrane resistivity on Redox system projected cost.

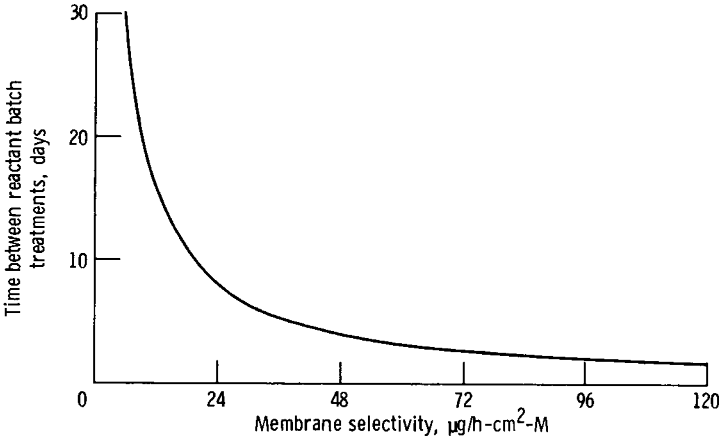

Figure 13. - Effect of membrane selectivity on reactant treatment interval needed to limit cross-mixing to 10 percent. System capacity, 5.0 MWh; reactant volume, 260 kl; batch volume, 15 kl.

as high as 75 mA/cm^2 must be attained. For acceptable efficiences at such current densities, cell resistivities must approach or be less than 1.5 ohm-cm^2.

The compromise value of ~20 μg/h-cm^2-M (ref. 8) for the other important membrane characteristic, selectivity, results in a gradual diffusional loss of each reactant into the other reactant system. If it is desired to prevent such cross-mixing from proceeding beyond some limit, two options are available: either begin operation with a great enough excess of reactants so that over the life of the system the decrease in the respective concentrations does not exceed the limit; or institute a batch treatment mode of operation whereby portions of contaminated reactants are periodically replaced by fresh quantities, and the contaminated quantities are then reprocessed. An estimate of the time interval between such batch treatments, as a function of the membrane selectivity and based on a simple diffusion model, is presented in figure 13. For the existing best compromise value of membrane selectivity of about 20 μgFe^{+3}/h-cm^2-M, the refurbishment interval for the specific example presented is about 9 days. In addition to being aesthetically less than pleasing, such a batch treatment mode of operation represents a cost burden which will become unacceptable as the time interval between refurbishments decreases.

Another characteristic of charged membranes in an electrochemical environment is the tendency of the electrolyte solvent to be transported preferentially in one direction. This net transfer results from the complex interactions between several system properties and is not easily analyzed. In principle, however, it should be possible to adjust the two reactant concentrations so that an isotonic situation would exist. This was accomplished several times in the laboratory, with cells being cycled for as long as 8 months with no net solvent transfer. However, this experience was not universal; success may depend on such things as the cycling regimen, the total reactant volume, the volume-to-area ratio, or other unknown parameters. For whatever the cause, when solvent transfer does begin, it often does not lead, as would be expected, to an isotonic situation and a cessation of transfer. In certain dramatic instances, one of the reactant systems was osmotically pumped nearly dry. As was the case with the cross-diffusion of reactant ions, the avoidance of this situation would require some mode of electrolyte refurbishment and an attendant cost penalty.

All of the foregoing is based on experience with, and the known properties of membranes at room temperature. In light of the apparent necessity for operation in the temperature range of 55° to 65° C to avoid difficulties charging the chromic ion, it became important to determine the effect of elevated temperatures on the critical membrane characteristics of resistivity and selectivity. To this end, membranes were acquired from various sources, primarily Ionics, Inc., RAI, and several Japanese producers, and characterized at Lewis. Selectivity was focused on because previous studies had shown (ref. 9) that, for the Ionics CD1L membrane, at least, a temperature increase from 25° to 65° C results in a resistivity reduction of 50 to 65 percent. It soon became obvious the temperature effect on selectivity was not as felicitous. Selectivity was determined by exposing each membrane sample to a 1 molar concentration gradient of ferric ion for 24 h, then measuring the quantity of ferric ion transferred. In table II the effect of temperature on selectivity over the range 25° to 80° C is presented for the standard Ionics membrane, a similar but "tighter" sample from Ionics, plus samples from the Electrotechnical Laboratory in Japan and from RAI. It can be seen that the selectivity in all cases is made dramatically worse by raising the temperature. Similar results were obtained for a group of anion exchange membranes supplied by RAI, shown in table III.

Based on the previously discussed sensitivity studies, from which it can be inferred that a selectivity of 20 $\mu g/h\text{-}cm^2\text{-}M$ is, at best, marginal for a realistic system, it follows that for membranes presently available raising the temperature has a disastrous effect. If diffusion is allowed to proceed unhindered at elevated temperatures, total cross-mixing of reactants would occur very rapidly. Batch-type refurbishments, on the other hand, would have to occur so frequently as to be economically unfeasible.

All of the above considerations associated with the effect of temperature on membrane characteristics led finally to a serious consideration of operation with premixed reactant solutions of identical composition in the discharged state, from the very outset. This mode of operation seemed potentially to offer some very attractive options, and its evaluation was begun during the final quarter of 1982.

OPERATION WITH MIXED REACTANTS

As was discussed in the preceeding sections, results in the areas of electrode and membrane development have made necessary a re-evaluation of the basic Redox system concept. Two significant aspects of that basic concept were the operation at temperatures in the 20° to 25° C range and the use of separators able to prevent significant cross-diffusion of the reactant metal ions. However, operation of iron-chromium Redox cells at normal ambient temperatures resulted in severe difficulties when attempting to charge the chromium half cells. It later was learned that by raising the operating temperature to 55° to 65° C these charging difficulties were eliminated (ref. 10). The next step, then, was to determine the effect of such temperatures on critical membrane properties. Measurements showed that a temperature increase from 25° to 65° C could reduce the resistivity by a factor of two or three but that the companion effect on selectivity was to make it worse, in some cases, by an order of magnitude. Such poor selectivity (i.e., such a high cross-diffusion rate) would require, in order to maintain some semblance of separation between the reactants, an electrolyte treatment procedure that would be unacceptably expensive.

All of this led to two options. The first was to attempt to develop an electrode catalyst that can alleviate at ambient temperatures the chromium reactant charging problems and at the same time to continue to attempt to improve membrane selectivity and resistivity, also at normal ambient temperatures. This approach is considered to have a low probability of success, but is being pursued, with regard to the electrode catalyst, at Case Western Reserve University and, with regard to membranes, at Ionics, Inc.

The second possible approach, the one actively being evaluated at Lewis, is to finesse the whole cross-diffusion problem by mixing the reactants beforehand. With this approach both reactant solutions, when the cell or system is fully discharged, are identical in composition, typically 1 M $FeCl_2$, 1 M $CrCl_3$, and 1 N HCl. When charged, the $CrCl_3$ in the positive (iron) reactant solution behaves as a nonparticipating species, as does the $FeCl_2$ in the negative (chromium) reactant solution.

The advantages accruing to this mixed-reactant mode of operation are

TABLE II. - THE EFFECT OF TEMPERATURE ON MEMBARANE SELECTIVITY

Membrane	Selectivity, µg Fe/h-cm^2-M, at -			
	25° C	45° C	65° C	80° C
CD1L-AA5-LC (27.5 NP) (standard)	23.1	83.4	168	501
CD1L-A5-LC (20 NP)	5.5	42.4	96	212
Electrotechnical Institute sample	77.0	184.3	293	659
RAI 1133-118-5	26.4	27.8	67	158

TABLE III. - EFFECT OF TEMPERATURE ON RAI ANION EXCHANGE MEMBRANE SELECTIVITY

Membrane	Selectivity, µg Fe/h-cm^2-M, at -		
	25° C	50° C	65° C
1133-287-1	29	97	163
1133-287-3	20	62	104
1133-239-1B	19	84	153
1133-239-1C	23	84	167
1133-239-2A	68	187	310
1133-239-2C	94	274	455
1133-239-2B	92	254	482
Ionics CD1L-AA5-LC	23	---	168

significant. By equalizing the total ion concentration of each reactant on both sides of the separator, the tendency for diffusional transfer to proceed is greatly diminished. Because cross-mixing then is much less a concern, membranes of a much looser structure, perhaps even microporous separators, can be used. The purpose of these primarily is to merely prevent or diminish convective flow from one half-cell to the other. Such membranes offer the added benefit of a significantly lower resistivity, which permits operation at higher current densities, and/or improved round-trip voltage efficiencies. Such membranes also can be expected to be less expensive than the highly selective types. Operation with mixed reactants also permits a simple technique to be employed if osmotic solvent transfer should occur or if there should be a loss of capacity due to partitioning of reactants: merely discharge the system and reblend the reactant solutions.

The above advantages for mixed-reactant operation are not totally without compensating penalties. Coulombic efficiencies are lower than those of cells with membranes having better selectivities because it is easier for the charged species of the two reactants to come into contact and undergo chemical discharge. Also, because of the dilution effect of the inert species on the activities of the respective reactant species, plus the thermodynamic effect of raising the cell or system temperature from 25° to 65° C, the cell open-circuit voltage at each state of charge is reduced from 50 to 70 mV. And finally, of course, is the obvious fact that the mixed reactant mode of operation requires more reactants and thereby costs more. However, it has been determined that reactant costs probably will be much less than had been previously assumed and will not militate against the mixed-reactant concept.

During the final quarter of 1982, experimental evaluation of the mixed reactant mode of operation at 65° C was begun (ref. 4). These tests were carried out using the standard 14.5 cm^2 laboratory cells. The reactants were heated as they flowed toward the cell through Pyrex tubes wrapped with sheathed Nichrome heating wire. The membrane generally used was a cation type designated ML-21, produced by RAI. This membrane was selected because previous screening had shown it to have a low resistivity and a very poor selectivity, on the order of 1000 $\mu gFe/h\text{-}cm^2\text{-}M$. Two types of chromium electrode catalyst were evaluated: the standard gold-lead composition and the new bismuth-lead formulation.

The experimental results from the brief period of testing at the end of 1982 were extremely encouraging. Figure 5 shows the voltage versus time (or, SOC) data for a complete constant-current cycle at 64.5 mA/cm^2. The ability to operate at this current density, especially during the entire charge portion of the cycle speaks eloquently of the advantage of operation at elevated temperature with a low-resistivity membrane. If such a test were to be attempted at ambient temperature using a selective membrane, the charging voltage would have reached an unacceptable level before 40 percent of the theoretical capacity was reached. Even if charging were to be completed in the taper current mode, the resultant voltage efficiency for the cycle would have been on the order of 60 percent, due to resistive losses, instead of the indicated 77.2 percent.

For this test coulombic efficiency was calculated from measurements with an integrating ampere-hour meter. Energy efficiency was obtained by integrating the areas under the charge and discharge curves and taking their ratio. Voltage efficiency was calculated from these measured values. A significant point to be made concerning these data is that although the total cell resistivity was about 1.74 ohm-cm^2, that of the membrane alone was only about 0.34 ohm-cm^2. The difference, of course, is the terminal contribution. It can, therefore, safely be assumed that, in a multicell, bipolar stack having highly conductive bipolar plates, the average cell resistivity would be much closer to 0.34 ohm-cm^2 than to 1.74 ohm-cm^2. From these sorts of considerations it is possible to project that complete Redox systems may be operated with energy efficiencies as high as 75 percent.

A very similar set of data is presented in figure 6. The main difference between the two experiments is that here the chromium electrode catalyst was bismuth-lead instead of gold-lead. The only difference of any note between the two sets of data is the reduced hydrogen evolution, 0.2 percent instead of 0.9 percent of charge capacity, for the bismuth-lead composition. The encouraging thing here is that there seems to be no difference at all in the polarization characteristics of the two types of catalyst.

Data for this second test cell provide insight into a system-related aspect of operating with mixed reactants. The cell was cycled automatically for 70 cycles. During this time there was a tendency for solvent to transfer toward the iron side of the system to the extent that on three occasions the cell was fully discharged, and the reactant solutions were reblended and then divided equally to the respective half-cell reservoirs. Polarization curves, taken at 50 percent SOC several times during this test period (fig. 14), show that such reblending of reactant solutions had no adverse effect on the activity of the bismuth-lead electrode catalyst.

Thus, although the amount of testing was quite limited in 1982, the results obtained from the experimental evaluation of the mixed-reactant mode of operation at elevated temperature were very satisfactory.

REACTANT COSTS

As mentioned earlier the viability of the mixed-reactant mode of operation is to some degree dependent on the cost penalty for the associated increased reactant requirements. During 1982, results became available from two contract studies of the projected cost for large-scale producton of the Redox reactants $CrCl_3$, $FeCl_2$, and HCl. These analyses were performed by Charles River Associates (ref. 11), a consultant firm with broad experience in hydrometallurgical processes, and by the Allied Chemical Co., a major producer of chromium chemicals. Each organization examined several process paths for the Redox reactants, starting with either chromite ore (Cr/Fe = 1.58 mass ratio), ferrochrome (Cr/Fe = 1.64), or the chemical intermediate, sodium chromate.

The results from these two independent studies were a very pleasant surprise. For the six processes examined, the highest projected cost was about equal to what previously had been considered to be an optimistic estimate. The remaining cost projections decreased to as low as 45 percent of the highest. The two sets of cost projections, adjusted to a common basis, are shown in table IV. The specific costs in dollars per kilowatt hour assume 80 percent utilization of reactants and an average cell discharge voltage of 0.9 V.

All of the processes based on a starting material of chromite ore or ferrochrome include provision for, at some point, separating the iron and chromium chlorides. This would, of course, be an unnecessary step, with an attendent

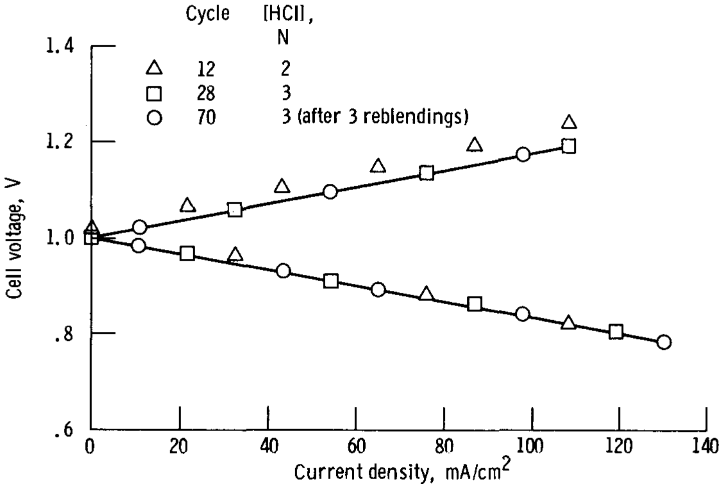

Figure 14. - Charge and discharge polarization data taken periodically during a 70-cycle test. Temperature, 65° C; mixed reactants; bismuth-lead catalyst for chromium electrode.

TABLE IV. - TOTAL COSTS FOR PRODUCTION OF REDOX CHEMICALS

[All costs in millions of dollars; 22,700 metric tons per year contained chromium plus equivalent $FeCl_2$ and HCl.]

(a) Allied Chemical Co. study

	Chlorination of prereduced chromite ore	Methanol reduction of sodium chromate	Electrolytic reduction of sodium chromate	Reductive chlorination of chromite ore
	Total investment, millions of dollars			
	$72.00	$71.50	$109.50	$275.00
Annual charges:				
Raw materials	$25.72	$33.56	$ 22.34	$ 31.20
Energy	1.72	11.50	21.46	1.72
Labor and related fixed capital charges	6.58 10.10	5.10 10.80	6.58 17.10	6.58 40.00
Expense	2.80	2.70	2.70	3.00
Return on investment	21.60	21.50	32.90	82.50
Total	$68.50	$85.16	$103.08	[a]$131.70
Total reactant cost:				
Per kg $CrCl_3$	$ .99	$ 1.23	$ 1.49	$ 1.91
Per kWh (unmixed reactants)	8.13	10.10	12.23	15.68
Per kWh (mixed reactants)	16.26	20.20	24.46	31.36

(b) Charles River Associates Study

	Hydrometallurgical production		
	From chromite ore	From ferrochrome	Reductive chlorination of chromite ore
	Total investment, millions of dollars		
	$69.34	$39.90	$95.33
Annual charges:			
Raw materials	$18.56	$36.70	$21.29
Energy	11.50	1.00	5.83
Labor and related fixed capital charges	2.65 10.42	1.60 4.70	3.62 14.44
Administrative expense	3.50	2.10	3.50
Return on investment (30 percent)	20.80	11.07	77.28
Total	$67.63	$58.07	$77.28
Total reactant cost:			
Per kg $CrCl_3$	$ .98	$ .84	$ 1.12
Per kWh (unmixed reactants)	8.05	6.90	9.20
Per kWh (mixed reactants)	16.10	13.79	18.39

[a] Includes credit for sale of $MgCl_2$ and $AlCl_3$, \$33.3.

unnecessary expense, if the desired final product were to be mixed reactants. Therefore, the specific costs for mixed reactants from these particular processes can be expected to be even less expensive than shown.

Of the processes examined, only those involving the reductive chlorination of chromite ore would require new or uncertain technology. The remaining processes are well understood and their associated cost estimates, therefore, should be quite reliable.

The cost estimates for Redox reactants, especially for the mixed reactant application, are certainly not insignificant, ranging from $14 to $31 per kWh. However, the most likely production routes are the two hydrometallurgical processes and the methanol reduction of sodium chromate process. The specific cost projections for these are in the range of $14 to $20 per kWh for the mixed reactants. Such reactant costs would not be expected to be prohibitive for the Redox storage sytem.

CONCLUDING REMARKS

Very significant achievements during 1982 have combined to further enhance the promise of the Redox system as a viable candidate for bulk electrical energy storage applications.

The present generation of membranes for Redox cells was shown to be unable to adequately keep separate the reactant species when cells are operated around 65° C, which is necessary in order to achieve adequate charging performance. This led to a serious evaluation of the mixed reactant mode of operation, which allows the use of nonselective, low-resistivity membranes. The results of preliminary testing in this operating mode were extremely gratifying. During constant-current cycles at 65 mA/cm^2, energy efficiencies greater than 70 percent were achieved. Concurrent studies of reactant production costs indicated that the added expense for mixed reactants is not prohibitive.

In the electrode area a new bismuth-lead catalyst has been developed that seems to have all the advantages of the standard gold-lead combination, plus a higher hydrogen overpotential and a more forgiving nature. Also, with regard to electrodes, a new understanding was reached concerning the causes of increased hydrogen evolution from gold-lead catalyzed chromium electrodes during prolonged operation. These causes are related to operational procedures, are not inherent to the electrode or to the Redox concept per se, and can be eliminated.

REFERENCES

1. Reid, M. A.; Johnson, D. A.: The Chemical and Electrochemical Behavior of the Cr^{+3}/Cr^{+2} Half Cell in the NASA Redox Energy Storage System. DOE/NASA/12726-17, NASA TM-82913, 1982.

2. Thaller, L. H.: Recent Advances in Redox Flow Cell Storage Systems. DOE/NASA/1002-79/4, NASA TM-79186, 1979.

3. Jalan, V.; Stark, H.; Giner, J.: Requirements for Optimization of Electrodes and Electrolyte for the Iron/Chromium Redox Flow Cell. DOE/NASA/0097-80/1, NASA CR-165218, Sept. 1981.

4. Hagedorn, N. H.: The NASA Redox Project Status Summary. Presented at the 5th U.S. DOE Battery and Electrochemical Contractors' Conference, (Arlington, Va.), Dec. 7-9, 1982.

5. Jalan, V.; Morriseau, B.; Swette, L.: Optimization and Fabrication of Porous Carbon Electrodes for Iron/Chromium Redox Flow Cells. DOE/NASA/0198-1, NASA CR-167921, July 1982.

6. Gahn, R. F.; et al.: Performance of Advanced Chromium Electrodes for the NASA Redox Energy Storage System. DOE/NASA/12726-15, NASA TM-82724, Nov. 1981.

7. Hodgdon, R. B.; and Waite, W. A.: Anion Permselective Membrane. DOE/NASA/0204-1, NASA CR-167872, Apr. 1982.

8. Ling. J. S.; and Charleston, J.: Advances in Membrane Technology for the NASA Redox Energy Storage System. DOE/NASA/12726-12, NASA TM-82701, 1980.

9. Gahn, R. F.; Johnson, J. A.; and Ling, J. S.: Single Cell Testing of the NASA Fe/Cr Redox System at Elevated Temperatures. Presented at the Electrochemical Society Meeting (Detroit, Mich.), Oct. 17-22, 1982.

10. Hagedorn, N. H.; and Thaller, L. H.: Design Flexibility of Redox Flow Systems. DOE/NASA/12726-16, NASA TM-82854, 1982.

11. Ammann, P. R.; Loreth, M.; and Harvey, W. W.: Study to Establish Cost Predictions for the Production of Redox Chemicals. DOE/NASA/0251-1, NASA CR-167882, July 1982.

BIBLIOGRAPHY

Ammann, P. R.; Loreth, M.; and Harvey, W. W.: Study to Establish Cost Predictions for the Production of Redox Chemicals. DOE/NASA/0251-1, NASA CR-167882, July 1982.

Gahn, R. F.; Johnson, J. A.; and Ling, J. S.: Single Cell Testing of the NASA Fe/Cr Redox System at Elevated Temperatures. Presented at ECS Meeting, (Detroit, Michigan), Oct. 17-22, 1982.

Hagedorn, N. H.; Hoberecht, M. A.; and Thaller, L. H.: NASA Redox Cell Stack Shunt Current, Pumping Power, and Cell Performance Trade Offs. DOE/NASA/12726-11, NASA TM-82686, Feb. 1982.

Hagedorn, N. H.: The NASA Redox Project Status Summary. Presented at the Fifth U.S. DOE Battery and Electrochemical Contractors' Conference, (Arlington, VA.), Dec. 7-9, 1982.

Hagedorn, N. H.; and Thaller, L. H.: Design Flexibility of Redox Flow Systems. DOE/NASA/12726-16, NASA TM-82854, 1982.

Hodgdon, R. B.; and Waite, W. A.: Anion Permselective Membrane. DOE/NASA/0204-1, NASA CR-167872, Apr. 1982.

Johnson, D. A.; and Reid, M. A.: Spectrophotometric and Electrochemical Studies of Chromium Species in Redox Solution. Presented at ECS Meeting (Detroit, Mich.), Oct. 17-22, 1982.

NASA Redox Storage System Development Project - Calendar Year 1980. DOE/NASA/12726-18, NASA TM-82940, Dec. 1982.

Reid, M. A.; and Johnson, D. A.: The Chemical and Electrochemical Behavior of Cr(III)/Cr(II) Half-Cell in the NASA Redox Energy Storage System. DOE/NASA/12726-17, NASA TM-82913, 1982.

Swette, L.; Jalan, V.; and Morriseau, B.: Optimization and Fabrication of Porous Carbon Electrodes for Iron/Chromium Redox Flow Cells. DOE/NASA/0198-1, NASA CR-167921, July 1982.

1. Report No. NASA TM-83469	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

NASA Redox Storage System Development Project
Calendar Year 1982

5. Report Date
October 1983

6. Performing Organization Code
776-72-41

7. Author(s)

8. Performing Organization Report No.
E-1784

10. Work Unit No.

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered
Technical Memorandum

12. Sponsoring Agency Name and Address
U.S. Department of Energy
Division of Energy Storage Systems
Washington, D.C. 10545

14. Sponsoring Agency ~~Code~~ Report No.
DOE/NASA/12726-23

15. Supplementary Notes

Annual report. Prepared under Interagency Agreement DE-AI04-80AL12726.

16. Abstract

Development was continued for iron-chromium battery operation at 65° C. Membranes that were adequate at 25° C were shown to be unacceptable at 65° C with regard to selectivity. This led to the elevated-temperature, mixed-reactant mode of operation, in which each reactant solution, when discharged, contains both ferrous and chromic chlorides. This operating mode allows the use of very low-resistivity membranes, resulting in high energy efficiencies at current densities. It also allows the use of very simple techniques to correct for solvent or reactant transfer through cell membranes. Screening of candidate catalysts for the chromium electrode led to the development of a bismuth-lead candidate having several attractive characteristics. 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.

17. Key Words (Suggested by Author(s)) Electrochemistry Redox Storage	18. Distribution Statement Unclassified - unlimited STAR Category 44 DOE Category UC-94cc

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 26	22. Price* A03

*For sale by the National Technical Information Service, Springfield, Virginia 22161