(NASA-TM-83677) NASA REDOX STORAGE SYSTEM DEVELOPMENT PROJECT Final Report (NASA) 48 p HC A03/MF A01 CSCL 10C
N85-12465
Unclas
G3/44 24445

DOE/NASA/12726-24
NASA TM-83677

NASA Redox Storage System Development Project

Final Report

Norman H. Hagedorn
National Aeronautics and Space Administration
Lewis Research Center

October 1984

Prepared for
U.S. Department of Energy
Conservation and Renewable Energy
Division of Energy Storage Systems

DOE/NASA/12726-24
NASA TM-83677

NASA Redox Storage System Development Project

Final Report

Norman H. Hagedorn
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

October 1984

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

CONTENTS

E-2125

NASA REDOX STORAGE SYSTEM DEVELOPMENT PROJECT - FINAL REPORT

Norman H. Hagedorn
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

The NASA Redox Storage System Technology Project received NASA and U.S. Department of Energy support, the latter being under Interagency Agreement DE-AI04-80AL12726 (previously EC-77-A-31-1002). Starting in 1979, project management was by the Sandia National Laboratories. The overall objectives of the project were to develop the Redox flow battery technology and to verify its suitability for utility and stand-alone applications.

From 1973 to 1982 the Redox system concept was based on 25° C operation and the use of anion exchange membranes as separators to prevent mixing of the acidified aqueous reactant solutions. New classes of such membranes were developed that, although not meeting the resistivity and selectivity targets established for economic viability, were adequate to show that the basic system concepts were valid. By 1978 the iron and chromium redox couples had been selected as the positive and negative reactants, respectively. A catalyst system, based on a gold-lead combination, was developed for the chromium electrode. This catalyst, in addition to being active for the chromium redox reaction, also inhibited hydrogen evolution. Analytical capabilities were developed to support the design of complete systems. These were used to study the various tradeoffs between shunt currents, reactant flow maldistribution, pumping power, reactant flow rates, and cell performance. System-level functions such as rebalancing, state-of-charge monitoring, and the use of trim cells were reduced to practice. This work culminated in the design, fabrication, and testing of a 1-kW, 13-kWh system. This system successfully validated the many desirable characteristics claimed for flow batteries, of which the iron-chromium system is a classic example.

Between 1980 and 1982 it was determined that certain cell performance problems were related to the existence of a chromic ion species that was not electrochemically active. It was further shown that increasing the temperature to 65° C would cause an equilibrium shift of this species to an active form. The remainder of the project effort was devoted to the exploitation of these new insights. The higher temperatures required for these reasons reduced membrane selectivity to the point that the use of separate reactants could no longer be considered. This, then, led to the mixed-reactant concept of operation, which in turn permitted the use of membranes with very low resistivities $(\sim 0.5 \text{ ohm-cm}^2)$. It then became possible to routinely operate single cells at current densities as high as 80 mA/cm^2 with energy efficiencies greater than 80 percent. Early system analyses indicated that this level of performance, coupled with the mass production of system components, would result in an economically viable Redox system. The actual achievement of these high levels of cell performance has greatly increased confidence that the Redox system, at a cost of about $75/kWh, could be a valid contender for storage applications. A new catalyst system using bismuth also was developed for the chromium electrode at elevated temperature. This material has several advantages over the gold-lead combination and has increased the operational flexibility of the system.

Standard Oil of Ohio (Sohio) has undertaken to continue the development of the Redox system. An exclusive patent license was obtained from NASA by Sohio. The transfer of the Redox technology from Lewis to Sohio is supported by the NASA Technology Utilization Office.

INTRODUCTION

The NASA Redox Storage System Technology Project was begun at the Lewis Research Center in 1973. The endeavor was an outgrowth of the fuel cell development work carried out at Lewis during the Apollo project. The in-house capabilities in the area of electrochemical systems, which resulted from this support of the Apollo project, were seen to be directly applicable to the terrestrial need for bulk storage of electrical energy. This need was newly perceived at that time and grew out of the oil embargo. The increase in the cost of hydrocarbon fuels, resulting from the embargo, placed a premium on the efficient use of these fuels. Adequate storage devices for off-peak electrical energy would allow the electric utilities to maximize the use of their most efficient base-load plants. Storage would also allow bulk purchasers of electricity to minimize their demand charges. Finally storage devices would permit the use of stand-alone intermittent energy sources such as photovoltaic cells and wind turbines.

In 1975 the Energy Research and Development Agency (ERDA) began support of the NASA Redox project. Subsequently, the Department of Energy, first under DOE/NASA Agreement EC-77-A-31-1002 and then later under Interagency Agreement DE-AI04-80AL12726 continued this support through 1982. The work at Lewis continued until early 1984, using previously authorized but uncommitted DOE funds.

The Redox project at Lewis was supported in-house by the Electrochemistry Branch of the Space Power and Technology Division. It was managed by the DOE Division of Energy Storage Technology through the Sandia National Laboratories' (SNL) Exploratory Technology Development Project. The objectives of the Redox project were to develop the Redox storage system technology and to verify its suitability, from both the technical and economic standpoints, for use in utility or stand-alone applications.

The Redox storage system and its development were based on an original concept that was patented at Lewis. After the selection of the iron and chromium redox couples as the positive and negative reactants, respectively, much of the ensuing effort focused on the development of suitable membranes, electrodes, and electrode catalysts. In parallel with this, system concepts were developed and scaled-up single cells were evaluated, as were multicell stacks of these scaled-up cells. The system-level work culminated in the assembly and testing of a 1-kW, 13-kWh system that was used as the storage device for a photovoltaic array. The system design work and associated cost analyses were supported by contracted modeling studies.

In 1981, at the direction of the SNL project manager, the system-level effort was halted in order to focus on difficulties with the basic electrochemical performance of the iron-chromium single cell. This redirection subsequently led to an understanding of the causes of the difficulties and to modifications for their circumvention. These modifications to the basic operating concept resulted in a threefold increase in the operating current density and a significant improvement in electrochemical energy efficiency, with no significant increase in projected system cost.

In the remainder of this report, the development of the iron-chromium Redox storage system technology is traced to its present state. The basic system concept is discussed in some detail. The development of the enabling technologies for the basic concept (e.g., membranes and electrodes) is reviewed, with considerable reference to existing reports. The discussion of the effort during the final several years of the project is somewhat expanded, to place proper emphasis on the significant advancements in Redox system performance during those years.

THE REDOX SYSTEM

In its original form, the iron-chromium Redox system represents the classic flow battery. The most significant characteristic of such a system is the complete solubility of reactants and products at all states of charge. This characteristic allows the storage of the reactants as acidified aqueous solutions in tankage that is external to the power-producing portion of the system. In the "two tank" version of a flow battery shown schematically in figure 1, each reactant is continuously circulated from its storage tank, through the groupings of single cells that make up the power-producing subsystem, and back to its storage tank. The flow rate of each reactant is always higher than the stoichiometric flow requirement, which would result in total reactant utilization in one pass through the battery cells. Typically, the cells would be arranged in series-parallel configurations of multicell stacks. In each stack the cells would be series connected in the bipolar mode, and the reactants would flow in parallel through the individual cells. As with any battery, each stack has terminals that allow for discharge into a load or for the acceptance of charge from an external power supply. In the iron-chromium Redox system the positive reactant is an aqueous solution of the ferric-ferrous redox couple, acidified with hydrochloric acid. The negative reactant is similar solution of the chromous-chromic couple. For both reactants the charge and discharge reactions involve simple one-electron transfers:

Positive electrode $$\mathrm{Fe}^{+3} + \mathrm{e} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Fe}^{+2}$$

Negative electrode $$\mathrm{Cr}^{+2} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} \mathrm{Cr}^{+3} + \mathrm{e}$$

In figure 1, the power-producing portion of the system is depicted as a single cell. In each such cell an anion exchange membrane separates the two flowing reactant solutions. The membrane ideally prevents cross diffusion of the iron and chromium ions, which would result in a loss of capacity, yet permits free passage of chloride and hydrogen ions for completion of the electrical circuit through the cell. These two desired characteristics of an ideal membrane - good selectivity and low resistivity - represent a stringent set of conditions.

In the Redox cell, each electrode is a porous carbon felt or graphite felt pad that is compressed between the membrane and the respective terminal plate.

ORIGINAL PAGE IS
OF POOR QUALITY

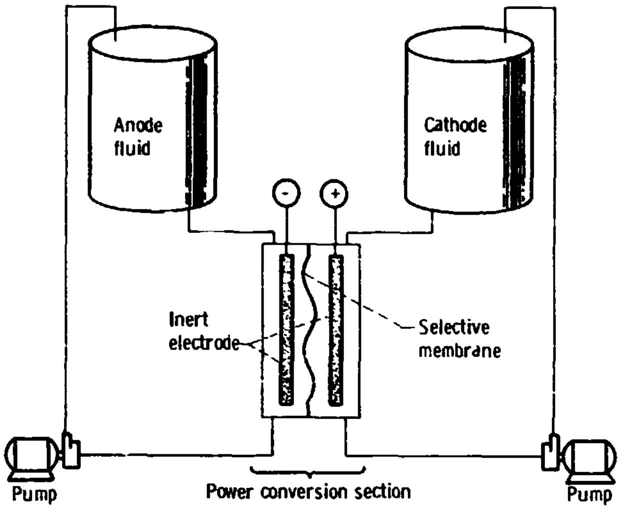


Figure 1. - NASA iron-chromium Redox flow battery.

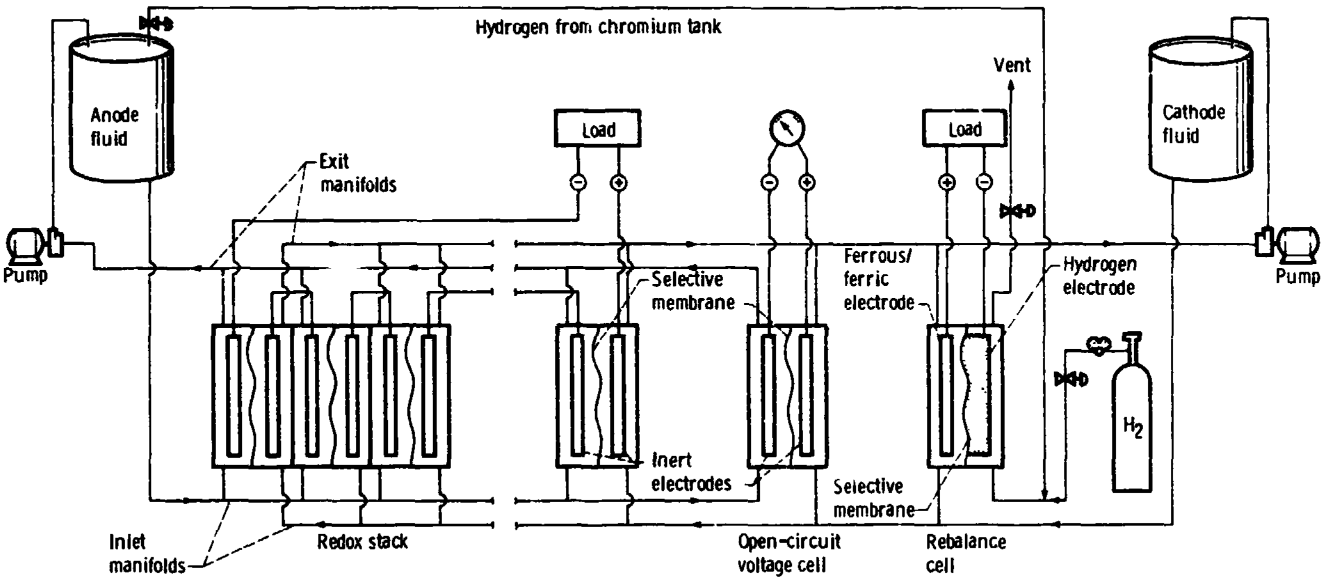


Figure 2. - "Full function" Redox system, including bipolar working cells, open-circuit cell, and rebalance cell.

The flow of each reactant solution is totally within the respective electrode structure, which provides an excellent mass-transfer environment. The carbon or graphite felt used for the chromium electrode is lightly catalyzed to promote the chromium redox reactions and to provide an overpotential for the hydrogen evolution reaction, which can otherwise occur at appreciable rates. Both porous electrodes serve as electron conductors and provide the sites at which the electrochemical redox reactions occur. The electrodes themselves, however, are inert both chemically and electrochemically in the working cell environment and undergo no physical or chemical changes.

Characteristic Advantages of Flow Batteries

Because the reactants of a flow battery are not confined within the individual single cells but are stored as solutions in external tanks, it is possible to independently size the energy storage portion (tanks plus reactants) and the power-producing portion (cell stacks) of the system. This in turn allows more efficient use of the stored reactants and also permits simple system modification and growth, both of which result in economic benefits.

Another advantage to the external storage of the reactants is that certain operational functions can be carried out at the system level instead of at the single-cell level. For example, since all cells are being supplied in parallel with reactants from common sources, insofar as their inlet reactant concentrations are concerned, all cells are at the same state of charge. This has several ramifications. First of all, one need not be concerned about individual cells getting out of balance with one another. Thus it is not necessary to monitor or manipulate individual cells. Instead any imbalance that does occur can be countered by dealing directly with the stored bulk of the reactants.

Another aspect of all cells always being at the same state of charge (with respect to their inlet reactants) is that different cells can be used in different ways, concurrently. For example, some can be accepting charge from an external source while others are being discharged. This makes it possible to use flow batteries as dc-dc transformers (ref. 1), as multivoltage output devices, and as storage for sources of intermittent and variable voltage such as wind turbines or solar photovoltaic arrays. In all cases the actual state of charge of the system is measured simply by determining the open-circuit potential between the stored reactants.

Another advantage inherent to this flow battery is that all of the electrode reactions occur in the solution phase. Since no phase changes take place at the electrodes, life-limiting processes such as slumping, shedding, or dendrite growth do not occur. Finally, the continuous flow of liquids through the cells of a flow battery serves to equalize their temperatures, eliminate hot spots, and provide a medium for system heat rejection.

The Full-Function Redox System

The advantageous characteristics of the flow battery concept can be incorporated into the design of cell stacks and systems. Figure 2 represents a stack that includes a bipolar series of working cells plus an open-circuit cell and a rebalance cell. The open-circuit cell is identical to the working cells in all respects but is isolated electrically so that it does not carry any current. The voltage of the open-circuit cell can be related directly to the system state of charge.

In the iron-chromium system there are two causes of chemical imbalance that can be treated electrochemically. The first cause is the evolution of hydrogen in the chromium portion of the system. This can occur electrochemically because of imperfect catalysis of the chromium electrode or chemically because of impurities that promote the reduction of water by chromous ions. The second cause of imbalance is the intrusion of air (oxygen) into either reactant system. In any case the result is always that the iron reactant becomes more highly charged than the chromium reactant. Thus the purpose of rebalancing is to discharge the iron reactant until it is at the same state of charge as the chromium reactant. This is easily accomplished by discharging an electrochemical cell (ref. 2) supplied with a stream of the iron solution as the positive reactant and a stream of hydrogen, from either the chromium tank ullage or an external source, as the negative reactant. A schematic of such a rebalance cell is presented in figure 3 (ref. 3).

Since it is possible to charge or discharge various cells in a flow battery at different rates without causing cell-to-cell imbalance, the use of trim cells becomes a feasible means for controlling the Redox system bus voltage. Trim cells are physically the same as the other working cells of a system, and reactants flow through them continuously, as with all other cells. However, these cells can be switched sequentially into or out of the electrical circuit as required, to maintain a relatively constant total system voltage. In this way changes in individual cell voltages can be accommodated as the system load or state of charge varies.

Design Considerations

Flow batteries such as the iron-chromium Redox system are subject to certain inherent inefficiencies. It is the responsibility of the designer of such a system to minimize the combined effect of these inefficiencies on system performance.

Shunt currents. - Figure 4 presents a schematic of a four-cell, bipolar stack of Redox cells. Included are the reactant inlet and outlet manifolds and the ports connecting the manifolds to the individual cell reactant cavities. The significant aspect of such a stack configuration is that electron-conducting bipolar plates at various potentials are interconnected through ion-conducting fluid paths. Provided that electrochemical reactions can proceed at the bipolar plate - electrolyte interfaces, self-discharge will occur through the conductive fluid paths. These self-discharge currents are referred to as "shunt", or "circulating", currents. A planform of a typical Redox flow plate (fig. 5) shows flow ports and manifolds. Mathematical analysis (ref. 4) shows that, for a given stack of Redox cells, the shunt currents are best reduced by increasing the ionic resistance of the flow ports. This can be done by increasing the length or reducing the cross-sectional area of the ports (ref. 5).

Pump requirements. - Unfortunately, increasing the ionic resistance of the cell ports also increases their flow resistance. Therefore all else being equal, as shunt-current losses are reduced, the parasitic pump power required

ORIGINAL PAGE IS
OF POOR QUALITY

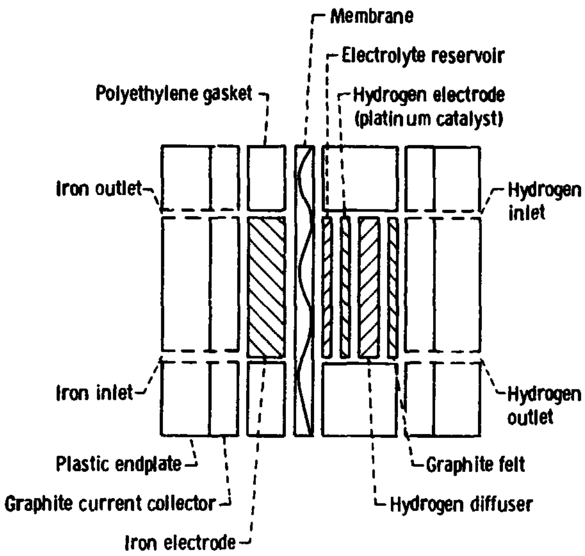


Figure 3. - Iron-hydrogen rebalance cell.

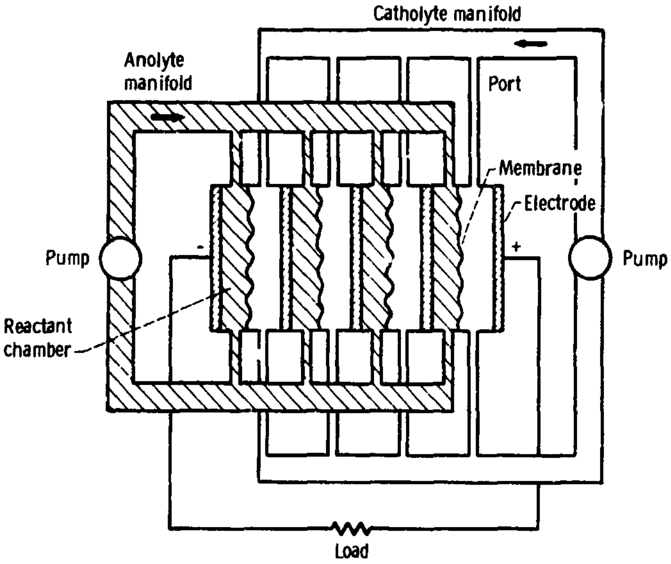


Figure 4. - Four-cell stack of Redox cells, showing shunt-current paths.

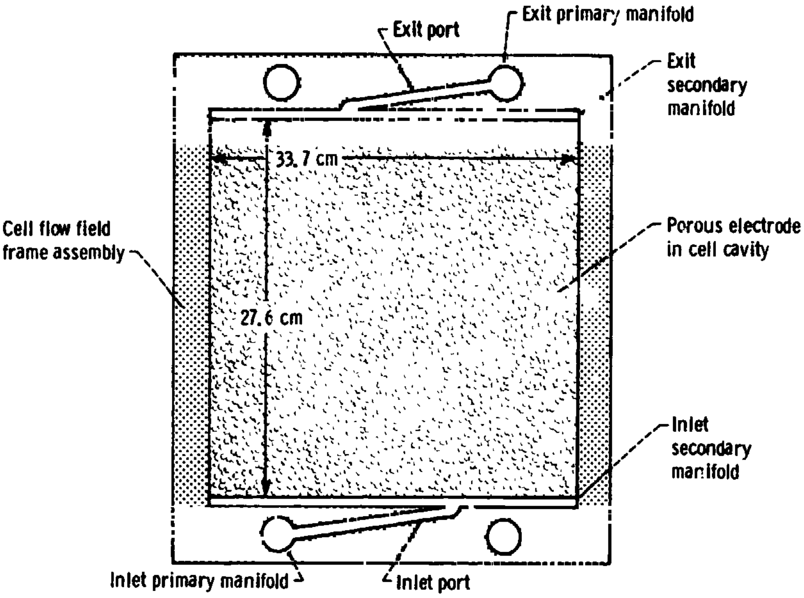


Figure 5. - Redox cell [illegible] plate, showing flow ports and manifolds.

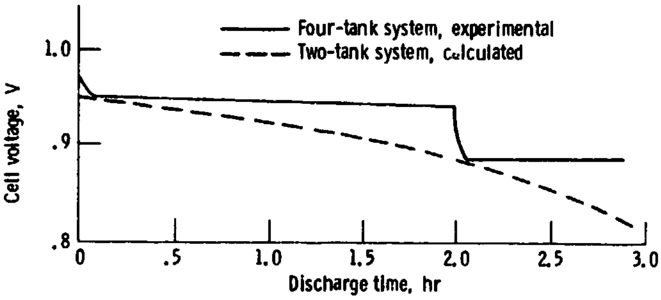


Figure 6. - Discharge performance of four- and two-tank systems. Current density, 14 mA/cm^2; flow rate, ~1.5 times stoichiometric; cell size, 320 cm^2.

to keep the reactants flowing is increased (ref. 6). Thus a tradeoff must be made between the two loss mechanisms represented by shunt currents and fluid pumping in order to minimize the sum of the losses. The critical design parameters are the single-cell flow port geometries and the reactant flow rates (ref. 7). There is some degree of latitude in selecting the design flow rates: the ideal lower limit, of course, would be the stoichiometric flow rate, but at this flow rate Nernstian corrections and concentration polarizations would impair working cell performance and efficiency (ref. 8). Therefore another tradeoff occurs, between the reactant flow rates (i.e., pump power) and the electrochemical performance of the working cells in the system. It thus can be appreciated that designing a flow battery to maximize system energy efficiency is a somewhat complex process requiring analytical models, experimental data, and iterative solutions.

Intrastack flow maldistribution. - In a typical stack of Redox flow cells the flow geometry is such that each reactant enters the stack at one end, flows through the cells in parallel from the inlet manifold to the exit manifold, and leaves the stack at the other end. If laminar flow is assumed throughout, analysis indicates that the reactant flow through the center cells of the stack will be less than that at the ends (ref. 7). Unless care is taken in cell and stack design, the central cells can be starved for reactant and suffer a performance loss. The critical design parameter is the ratio of the flow resistance of the flow port to the flow resistance of the manifold segment connecting adjacent cells: the greater the ratio, the more uniform the flow distribution. There are several ways to deal with intrastack flow maldistribution. One would be to use a great enough flow rate so that even the central cells of a stack would receive adequate flow. Another would be to increase the flow-port flow resistance of the cells. Both of these approaches increase the pump power requirement of the battery system and thus add even more complexity to the process of system design.

Reactant backmixing. - Another efficiency penalty is associated with the classical flow battery (fig. 1) because of its two-tank configuration. In discharge mode, for example, partially depleted reactants leaving the cells are continuously returned to their respective tanks, where they can mix with less-depleted reactants (assuming that significant mixing does occur in the tanks). Therefore the reactants leaving the tanks and entering the cells at any time are at a lower concentration and activity than would be the case had this mixing not occurred, and the cell voltages are correspondingly less. One way to circumvent the loss of performance and efficiency associated with this continuous reactant dilution would be to use two tanks for each reactant (ref. 2), with one tank for each reactant serving as the receiver for that reactant as it exits the cells. For a system operating at constant current in this four-tank mode, voltage would remain constant until all of the reactants had passed through the cells and been collected in their respective receivers. Flow could then be reversed and the constant-current discharge would proceed at a lower constant voltage. At all times, however, the system voltage would be greater than would be the case for the two-tank operating mode (fig. 6). Analysis indicates that a benefit of 3 to 5 percent in energy efficiency can be obtained in this way, at the expense of increased system complexity and cost.

The preceding discussion of the classic flow battery, as exemplified by the Redox iron-chromium system, shows the desirable characteristics and capabilities that are unique to flow batteries. However, to reap the full benefit of these inherent advantages, great attention must be given to cell, stack, and system design. Otherwise the inefficiencies that are also inherent in such systems can fully negate the advantages. In a later section a 1-kW Redox flow battery system designed, assembled, and tested at Lewis is discussed. The final design of this system gave attention to all of the characteristics of flow batteries that have been discussed here.

DEVELOPMENT OF AMBIENT-TEMPERATURE REDOX STORAGE SYSTEM

The basic Redox system was conceived at Lewis in 1973 (ref 9). At that time it was specified that system operation would be at or near ambient temperature. During the next 7 years the concept was brought from a very small proof-of-concept demonstration cell to a fully functional 1-kW, 13-kWh system that operated in conjunction with a photovoltaic array. The development process involved both in-house and contract efforts in the areas of electrodes, membranes, system components, cell and stack scaleup, system analyses and cost studies. This development process is traced herein.

Electrodes

Several factors had to be considered with regard to flow-cell electrode development. The first obviously was the choice of the redox couples to be used. In parallel with this determination though was the selection of the electrode substrate material, its physical form, and the associated cell structure and reactant flow regime. Finally it was necessary to ascertain whether catalysts would be required for any of the redox reactions and, if so, to bring about their development.

Redox couples. - The earliest cell testing at Lewis was based on the Fe^{+3}/Fe^{+2} couple as the positive reactant and the Ti^{+3}/TiO^{+2} couple as the negative (ref. 10). This pair soon was shown to be less than ideal, primarily because of low cell voltage, poor negative electrode kinetics, and TiO_2 solubility ity problems. Nonetheless, it did serve as a starting point for cell development and for establishing testing procedures. In the meantime, a contract effort at Giner, Inc., undertook the systematic screening of redox couples by the rotating-disk procedure (ref. 11), using gold and vitreous carbon as the working electrodes. The results of this work showed Fe^{+3}/Fe^{+2} and Br^-/Br_3^- to be attractive as positive reactants, and Cr^{+2}/Cr^{+3} and $Cu(NH_3)_2^{+1}/Cu(NH_3)_4^{+2}$ to be attractive as negative reactants, when the measured exchange currents were used as criteria. The iron couple was selected by Lewis over the bromide couple for reasons of safety, reactant vapor pressure, and materials compatibility. This choice then precluded the copper couple as the negative electrode because of its alkalinity. The copper couple also suffered from poor solubility. Therefore it was decided to undertake the development of an iron-chromium Redox flow battery.

Substrates. - Another aspect of the initial Giner contract was the evaluation of several different electrode structures and cell configurations. The electrode structures included metal screens and sheets, carbon and graphite blocks and cloths, and screens and carbon papers activated with Teflon catalyst mixtures. The cell configurations included electrodes adjacent to the membrane with flow behind; electrodes adjacent to the terminal blocks with flow in front; and cavity-filling electrodes through which the reactants flowed. Redox couple screening at Giner, Inc., indicated that each couple had a favored cell configuration. At Lewis, several electrode structures and cell configurations were also being evaluated. These included a catalyst that was solvent bonded to the membrane, activated planar surfaces (ref. 12), and cavity-filling carbon/graphite cloths and felts. Generally cell structures in which the reactant streams flowed entirely within the electrodes gave superior performance because of the induced turbulence and enhanced mass transport arising from such a flow environment. At Lewis, multiple layers of carbon or graphite cloth were initially used in laboratory cells, but these cloths were soon replaced with carbon or graphite felts. With regard to the iron redox couple, there were never any difficulties with the use of carbon or graphite felts as electrodes. These materials, after moderate cleaning in acid or caustic, provided active surfaces for the highly reversible iron redox reactions. Such was not the case for the chromium redox reactions. As catalyst systems were being developed and evaluated for the chromium reactant (discussed later), it became apparent that the successful catalysis of an electrode was highly dependent on the characteristics of the felt substrate. The major difficulty arose from variations between felt lots that ostensibly were the same, and even from variations within a given lot. Considerable effort was expended during the subsequent years by Lewis and Giner, Inc., to develop specifications for carbon and graphite felts that would form acceptable chromium electrodes when catalyzed. This endeavor was made easier by the cooperation of the supplier of the felts, Fiber Materials, Inc. (FMI). The major result of this effort was to show that the optimum felt resulted when the rayon precursor was pyrolyzed at about 1650° C. This determination was based on the measured rate of hydrogen evolution from the chromium electrode of a working cell during a standardized cycle (fig. 7). This work is discussed in detail in references 2, 13, and 14.

Another aspect of the endeavor to assure reproducible production of well-behaved chromium electrodes was the development of pretreatments to further normalize the felt substrates before catalysis. Such pretreatment was deemed necessary to counter felt hydrophobicity and to deal with possible active surface radicals that could affect the subsequent catalysis processes. Nitric acid and potassium hydroxide were evaluated as cleaning agents, and heat and vacuum impregnation were tested as aids to the pretreatment process. This work, discussed in detail in references 13 to 17, resulted in standardized procedures that greatly enhanced the ability to fabricate catalyzed chromium electrodes of reproducible performance.

Catalysts. - As mentioned earlier, carbon and graphite felts were shown to provide excellent activity for the iron redox reactions. The chromium reactions on carbon and graphite, however, required high polarizations in order to proceed in working cells. Therefore Giner, Inc., was contracted to screen possible catalyst materials for the chromium reactions. These materials, 26 in all (ref. 18), included metals and metalloids, alloys, plated surfaces, and Teflon-bonded structures. Also five organic materials were evaluated as possible hydrogen evolution inhibitors, but these proved to be ineffectual. Evaluations were all based on linear sweep voltammetry in stirred solutions.

No single material tested gave both acceptable anodic and acceptable cathodic performance for the chromium redox reactions. However, gold served well as an anodic electrocatalyst and lead was a good catalyst for the cathodic reaction, having in addition a high hydrogen overpotential. Gold-lead combinations were therefore evaluated, and they exhibited the good characteristics of the two constituents without the disadvantages shown by them individually (ref. 18).

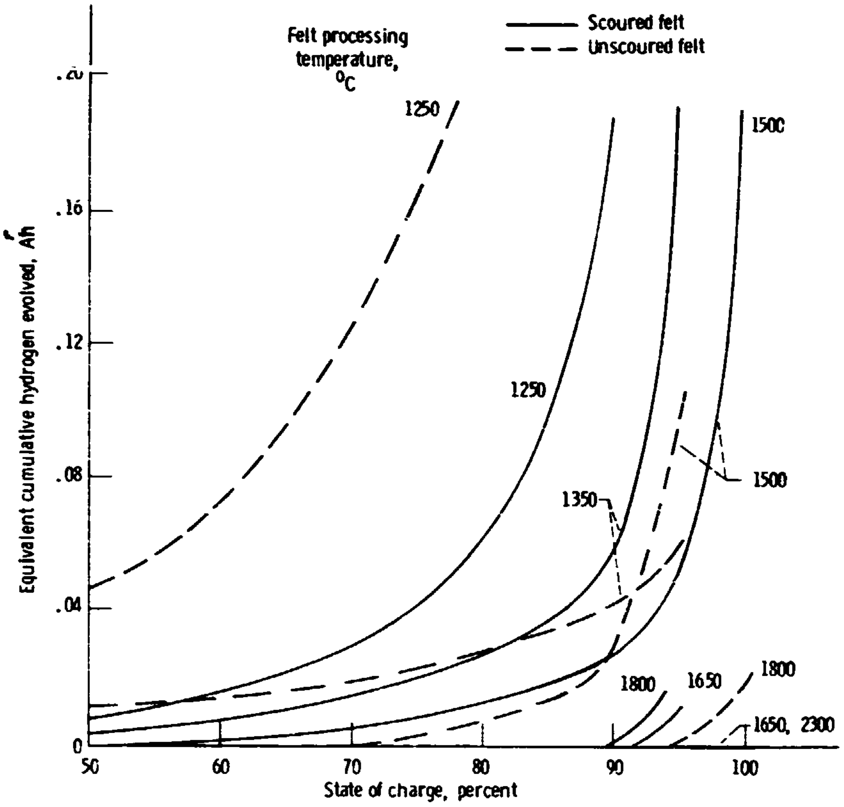


Figure 7. - Hydrogen evolution during charging of chromium electrode, showing effect of felt processing temperature.

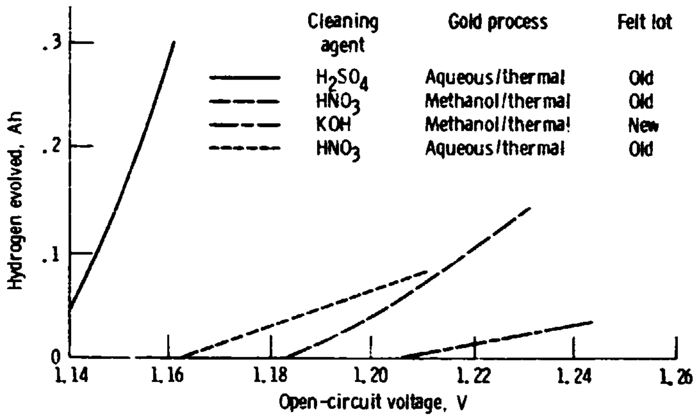


Figure 8. - Hydrogen evolution during charging of chromium electrode, showing effect of electrode preparation and catalyst application technique.

The gold-lead catalyst can be formed in several ways, including sequential electrodeposition of the constituents, simultaneous electrodeposition, and thermal decomposition of a gold salt followed by electrodeposition of lead. Work by Lewis and by Giner tended to show that the last technique produced electrodes of acceptable performance most consistently. Subsequent work was directed toward refining the gold application technique and evaluating variations in the constituent loadings. The net result of these efforts was a standardized process for the preparation of gold-lead-catalyzed felts for use as chromium electrodes (refs. 13, and 15 to 17). Work by Yeager and colleagues at Case Western Reserve University has shown the probable structure of the gold-lead combinations to be the result of underpotential deposition of the lead on the gold.

One major criterion by which catalyzed chromium electrodes were evaluated was the rate of hydrogen evolution during the charging (cathodic) reaction. Figure 8 gives an indication of the progress that was made during these studies in reducing hydrogen evolution. The various curves show the effects of the felt substrate, the cleaning process, and the gold application technique on hydrogen evolution.

In a wide range of tests the gold-lead catalyst proved to be stable and durable. One 320-cm^2 cell was cycled for 18 months, undergoing 20 000 accelerated cycles and 3000 standard cycles with no apparent loss of electrode activity (fig. 9). During this testing period the cell was several times driven into deep reversal without damage (ref. 17). Other tests, though, showed that the ability of the catalyst to inhibit hydrogen evolution could be lost if the chromium electrode were exposed to a chemically oxidizing environment after some period of normal usage. Such oxidation could result from air (oxygen) or ferric ion intrusion into the chromium system (ref. 19). Neither of these occurrences would be expected in normal operation.

The gold-lead combination thus became the standard chromium electrode catalyst for the ambient-temperature Redox system. Electrodes catalyzed as previously described were used successfully in the 1-kW Redox system. Criteria also were developed by which cyclic voltammetry could be used to evaluate these electrodes before their installation in the cell stacks (ref. 16).

Membranes

The membrane to be used in the ambient-temperature Redox cell had to perform two critical functions: prevent, almost totally, the cross mixing of the two reactant species and at the same time allow free passage of other ions such as protons and chloride ions to complete the electric circuit through the cell. These required properties - good selectivity and low resistivity - unfortunately tend to be mutually exclusive: steps taken to improve one property inevitably cause the other to deteriorate. Other requirements were that the membrane be physically strong, chemically inert in the cell environment, and inexpensive.

At the very beginning of the Redox project, several commercially available membranes were evaluated. Many of them were incompatible with the Redox cell environment. Those that were physically and chemically stable failed to provide acceptable resistivity and selectivity (refs. 20 and 21).

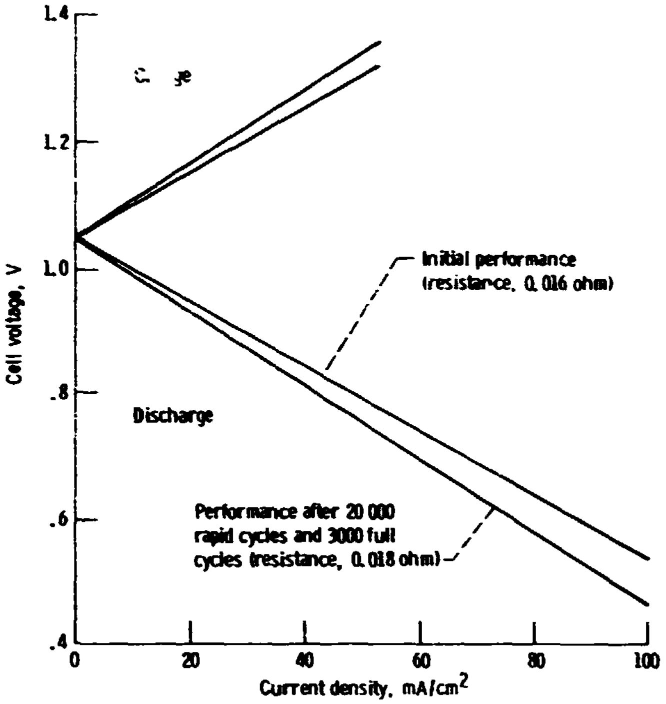


Figure 9. - Redox single-cell performance before and after 18 months of cycling. Cell size, 320 cm^2.

Therefore, early in the program Ionics, Inc., was contracted to develop membranes specifically for the Redox system. It was assumed from the beginning that such membranes would require an anion exchange character in order to inhibit cross diffusion of the reactant cations. Giving the membranes a high ion-exchange capacity (IEC) would also enhance membrane conductivity. Therefore Ionics, Inc., first investigated and evaluated 15 membrane systems, each comprising a different combination of resin and ion exchange group (ref. 22). These combinations possessed a wide range of both strong-base and weak-base ion exchange groups, the latter including examples of primary, secondary, and tertiary amines. Membrane constituents included 2-vinyl pyridine, ethylene glycol dimethacrylate, vinylbenzyl chloride (VBC) post-aminated with diethylenetriamine and dimethylamioethyl methacrylate (DMAEMA). Methods of membrane fabrication included bulk polymerization followed by activation, if needed; film casting; and direct activation of preformed films. These initial evaluations (discussed in detail in ref. 22) resulted in considerable improvements in all of the critical membrane characteristics. Nonetheless considerable improvements were still required.

The next level of development was therefore to select the most promising candidate membrane systems and endeavor to further improve them (ref. 23). These systems were prepared by bulk polymerization of the liquid monomers on synthetic fabric backing. Variations in the critical synthesis parameters of cross-link density, monomer ratio, and solvent composition were examined. This advanced screening effort identified the two most effective candidate membrane types, designated "CP4L" and "CD1L." As these membranes were further refined and characterized, the contractor was more and more forced to come to grips with the basic technical problem: improvements in selectivity generally are accompanied by increases in resistivity (ref. 24). For the CP4L type of membrane, not only was the resistivity relatively high upon initial exposure to acidified ferric chloride solutions, but it proceeded to increase with extended exposure. Primarily on the basis of this characteristic of the CP4L, the CD1L was selected as the focus for further developmental work. This membrane is a copolymer of VBC as the backbone and DMAEMA as the cross-linker, on a woven modacrylic substrate. The VBC/DMAEMA ratio was 1/2 and the nonpolymerizable (NP) solvent content was about 25 percent.

Subsequent efforts by Ionics, Inc., consisted largely of variational studies and fine tuning of the CD1L composition and fabrication technique to optimize the membrane characteristics (refs. 25 and 26). The resulting membrane, which became the standard for use at Lewis, was designated CD1L-AA5-LC (27.5 NP). Its pertinent performance characteristics (ref. 2) were resistivities of 4.2 ohm-cm^2 in 0.1 N HCl and and 2.6 ohm-cm^2 in a working iron-chromium Redox cell and a selectivity of about 20 μg Fe^{+3}/h cm^2 M. This membrane type had excellent stability in the ambient-temperature Redox cell environment, as evidenced by analyses performed on a 320-cm^2 membrane after 18 months of in-cell cycling at Lewis (refs. 2 and 26). There was virtually no change in water content, IEC, or resistivity.

In parallel with its membrane development work, Ionics, Inc., evolved fabrication techniques that led to yields of 95 percent for CD1L membranes as large as 107 by 51 cm (42 by 20 in.) and for batches as large as the 200 46 by 46 cm (18 by 18 in.) membranes prepared for the 1-kW system at Lewis.

The selectivity and resistivity given here for the optimum CD1L membrane represent the best possible tradeoff between these two important characteristics and made the CD1L superior to all other types evaluated during most of the ambient-temperature Redox system development. However, near the end of this development phase, RAI Research was able to produce radiation-grafted anion exchange films with similar performance characteristics. These characteristics, although the best attainable, were still a long way from the goals of 5 μg Fe^{+3}/h cm^2 M and 1 ohm-cm^2 then deemed desirable. Nonetheless, as evidenced by the Lewis 1-kW system, an ambient-temperature Redox system using the available membranes was a technically viable storage system.

With the exception of some development work on heterogeneous membranes early in the Redox project (refs. 20 and 27), the membrane effort at Lewis consisted primarily in the evaluation of membranes from Ionics, Inc. These evaluations, discussed in references 12 and 28, consisted of screening tests such as visual examination for pinholes and the measuring of selectivity, followed by cycling in working Redox cells. In general, there was a good correlation between results at Lewis and measurements made at Ionics, Inc.

One membrane characteristic, the significance of which was not really appreciated until the testing of larger cells and stacks of cells began, is the osmotic transfer of solvent from one reactant system to the other. This transfer would normally be expected to diminish and then cease as concentration gradients developed between the reactant systems. However, because of the complex interplay of several transport phenomena (ref. 12), the solvent transfer continued in some cases until near depletion of one of the reactant systems, typically the iron (positive) system. It was shown that electro-osmosis, using a special electrochemical cell, could be used to counter the transfer but would result in an efficiency penalty. On occasion it was also shown that the respective reactant concentrations could be initially adjusted in such a way that that solvent transfer never began (ref. 19); but this apparently was a pseudo-equilibrium that could be upset quite easily. The solvent transfer difficulty, typical of all membranes, especially those bearing charge sites, thus introduced an operational requirement for reactant volume maintenance for long-lived systems. The amount of solvent transfer in the 1-kW system was notable.

Scaleup: The Ambient-Temperature 1-kW Redox Storage System

When the critical elements of the Redox single cell - the reactant couples, the electrodes, and the membranes - had become fairly well defined, the next steps in the development process required the scaleup and testing of single cells and multicell stacks. The scaleup process proceeded from the 14.5-cm^2 active area laboratory cell to 320-cm^2 and finally 930-cm^2 cells (ref. 5). A major element of concern with regard to these larger cells was whether the reactant flow would be uniformly distributed within the respective porous electrodes. If not, "dead spots" would be expected to occur, resulting in the development of concentration polarizations. Such polarizations were not observed with these cells over the normal operating ranges of current density, depth of discharge, and reactant flow rates, thus indicating good reactant flow distribution.

Most of the early multicell stacks were composed of the 320-cm^2 cells, although one five-cell stack of 930-cm^2 cells was successfully evaluated. One of the more significant aspects of the multicell stack testing was the comparison of the measured shunt-current losses with the losses predicted by a mathematical model. These losses were measured by charging the stack at a fixed voltage until the charging current tapered down to a steady-state value. This steady charge-acceptance rate just balanced the self-discharge rate caused by shunt currents. Discrepancies between the measured and calculated shunt losses indicated the degree to which the actual stack geometry differed from the model. These studies led to a series of design changes which, as shown in table I, brought the multicell stack configuration into close conformance with the model and minimized the self-discharge rate.

After these five-cell stack studies, the next level of scaleup was a 14-cell stack of the 320-cm^2 cells. This stack, used as a demonstration device, was a full-function unit containing trim cells, a charge indicator cell, and a rebalance cell in addition to the standard working cells. A photograph and a stack schematic are shown in figures 2 and 10 (ref. 29).

The largest stacks assembled during the course of the Redox project were the 39-cell stacks (320-cm^2 cells) for the 1-kW system. Eight of these stacks were assembled and evaluated. The first set of four stacks was subject to unexpectedly high hydrogen evolution rates. Analysis of the problem led to an improved method of catalyzing the chromium electrodes, and an electrochemical analytical technique for screening the electrodes before stack assembly (ref. 16). These procedures, applied during the preparation of the second set of four stacks, reduced hydrogen evolution rates to fully acceptable levels. These latter four stacks subsequently became the power section for the 1-kW system.

All of these scaleups, whether in cell size or in the number of cells per stack, were successful: there was no loss in intrinsic cell performance (i.e., no development of unexpected polarizations) attributable to the effects of scaling up.

The design specifications for the 1-kW Redox storage system are given in table II. This system (fig. 11) and its evaluation are discussed in detail in references 12 and 30. The system was designed to serve as the storage device for a photovoltaic array, thus simulating a remote, stand-alone application. The main focus of the evaluation of this system was to investigate the interactions at the interfaces between the array, the storage system, and the load. The intention was that the array controls and the Redox system controls never be allowed to work at cross-purposes. The respective control concepts were simple, being based on meter-relay devices, and no conflicts occurred.

The evaluation of the various inefficiencies and loss mechanisms during system operation gave considerable insight regarding possible efficiency improvements for subsequent, larger systems. These improvements would result from design changes, concept modifications, and altered operating modes and would require no technological breakthroughs.

The ability of a flow battery to use trim cells was quite strikingly demonstrated. The Redox system was able to discharge to a load at 120 V while simultaneously accepting charge at a lower voltage from the array during periods of low insolation. It thus acted as a dc-dc (ref. 1) transformer as well as a storage device. The system also recovered from inductive load surges within 50 ms. Several different modes of connecting the array to the Redox system were examined in terms of advantages and disadvantages. The mode to be chosen would depend on the particular application under consideration.

TABLE I. - REDUCTION OF SHUNT-CURRENT LOSS (TAPER CURRENT) BY CELL DESIGN CHANGES: FIVE-CELL STACKS, 1.20 V/CELL

Configuration	Taper current, mA
Original	2000
Bipolar-plate manifold holes insulated from fluids	140
Membrane manifold holes insulated from fluids	28
Membranes insulated from fluids in port slots	12
Mathematical model	7

TABLE II. - NOMINAL DESIGN SPECIFICATIONS FOR NASA LEWIS PREPROTOTYPE 1-kW REDOX STORAGE SYSTEM

Gross power, W	1260
Nominal net power, W	1000
Voltage, V dc	120±5
Number of stacks	4
Number of cells per stack	39
Number of trim packages (six cells each)	10
Depth-of-discharge range (utilization), percent	80 - 20 (0.60)
Reactant volume (each), liters (U.S. gallons)	700 (186)
Reactant energy density (end of life), Wh/liter	14.5
Cell active area, cm^2	320
Nominal current density, mA/cm^2	30
Reactants	1 M $FeCl_3$, 2 N HCl 1 M $CrCl_2$, 2 N HCl
Reactant flow rates (nominal), cm^3/min cell	100-150
Parasitic losses, W:	
Pumps (efficiency, percent)	120 (15)
Shunt power	120
Number of rebalance cells	5
Number of charge-indicator cells	1

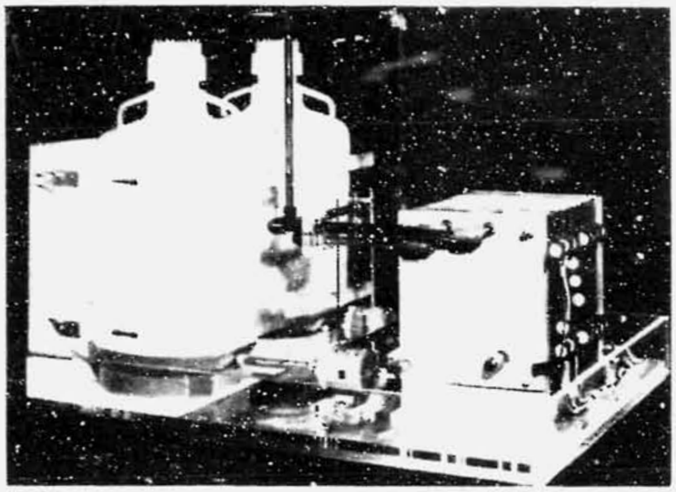


Figure 10. - Full-function Redox system demonstration unit.

Figure 11. - 1-kW, 13-kWh Redox system.

The evaluation of scaled-up single cells, multicell stacks, and complete systems revealed no inherent difficulties with the basic Redox flow battery concept. Rather, the testing served to verify that the system was uncomplicated, simple to operate, and extremely flexible in terms of the available design options and the applications that might be accommodated.

Rebalance Cells

The development of rebalance cells was not a major part of the Redox project. As discussed earlier, the purpose of these cells is to restore the two reactant systems to the same state of charge after imbalance has occurred. This rebalancing was easily accomplished by using two very well-behaved electrodes - an iron cathode identical to that in the Redox working cell, and a hydrogen anode typical of hydrogen-oxygen fuel cell technology. However, the hydrogen electrode was always subject to a slow loss of performance due to flooding, because the membrane allowed osmosis of solvent from the adjacent flowing aqueous iron reactant stream. Generally, this performance loss was reversible through the occasional use of an acid flush of the hydrogen electrode cavity followed by drying with a nitrogen purge.

A more serious difficulty arose with regard to the stability of the platinum catalyst of the hydrogen cell. Small rebalance cells were used routinely in the testing of Redox single cells in the laboratory to monitor the hydrogen evolution from the chromium electrodes. It was noted that often, after about 4 months of testing, this hydrogen evolution rate would start to increase significantly. This was always attributed to a deterioration of the Redox cell's chromium electrode. However, when testing at 65° C began (discussed in later sections), it was noted that the hydrogen evolution began to increase almost immediately. An x-ray analysis of the component parts of the working cells revealed the presence of platinum. Thus it was learned that it was possible for the hydrogen electrode catalyst, platinum, to dissolve anodically, migrate into the flowing iron stream, and then work its way through the working cell membrane to the chromium half-cell, where it was reduced. The platinum metal could then continuously catalyze the reduction of water by chromous ions, evolving hydrogen.

The anodic dissolution of the platinum has several causes. One is excessive polarization of the hydrogen half-cell during discharge of the rebalance cell. Another is the diffusion of ferric ions through the membrane when the cell is in a standby mode. In principle, these conditions are easily avoided. The use of a reference electrode would make it possible to monitor the performance of the hydrogen electrode and avoid excessive polarization. When in standby, a continuous trickle charge of the rebalance cell would cathodically protect the hydrogen electrode catalyst. The effect of these steps on system cost or efficiency would be negligible, but they would represent an additional operational requirement.

Several approaches were evaluated to totally remove the platinum from the system. The first was to replace the platinum electrode catalyst with tungsten carbide (WC) This material did show some initial electrochemical activity when used in a rebalance cell but soon passivated, probably because of electrode flooding. It is believed that a small development effort would result in a WC-catalyzed hydrogen electrode of sufficient activity for rebalancing purposes.

The other approach, which was adopted for laboratory tests near the end of the project, embodied a cell in which the hydrogen-consuming anode was replaced by a chlorine-generating anode. The electrode material was a porous carbon felt identical to that in the iron half-cell. The reactant supply for the anode of this cell was a small, separate stream of 3 N HCl that also contained 1 M $FeCl_3$ and 1 M $CrCl_3$ to minimize osmotic effects. In operation, electrical energy was supplied to the cell to bring about the evolution of chlorine and the cathodic reduction of ferric ions. Makeup HCl was occasionally added to replace the chlorine generated in the rebalance cell and the hydrogen evolved from the working cell. Optionally, the chlorine and hydrogen could be recombined catalytically in the presence of ultraviolet light. The use of such a rebalance cell would introduce a system efficiency penalty and increased operational costs. Nonetheless, these penalties should not have a marked effect on overall system cost and efficiency and could be more acceptable than the threat of system contamination by platinum associated with the hydrogen-iron rebalance cell.

The performance of the iron-chlorine rebalance cell was excellent. The ability of this cell to restore full capacity to a working cell is shown in figure 12. Because it is electrically driven, it allows precise control of the balance process - a definite advantage. As discussed here, several options are available for rebalancing the Redox system reactants. Each has its own unique advantages and disadvantages. A moderate development effort should result in the choice of the best approach, with no serious effect on system cost or efficiency.

Cost Analyses

The scaled-up single cells, the multicell stacks, and the complete Redox system assembled at Lewis for evaluation were expensive. The reasons, of course, are typical of those for all developmental hardware: small quantities of materials are used; requirements are overspecified; tolerances are excessively tight; the design does not facilitate assembly; some components are, themselves, developmental and include the costs of development; and all operations are carried out by hand. In spite of all this, it is necessary, in order to establish the viability of a device such as the Redox system, to verify not only the technology but also acceptable economics for the device.

For this latter purpose several contract studies were carried out during the course of the Redox project to estimate the cost of producing Redox hardware and reactants in a mass-production environment. United Technologies Corporation (UTC) was selected for the hardware cost study because of their long experience in the production of hydrogen-oxygen fuel cell systems. These electrochemical devices have many component similarities to flow batteries. For the study of reactant production costs, two contractors, the Allied Chemical Co. and Charles River Associates (CRA), were selected. The former company is a major producer of chromium chemicals; the latter company, a consulting firm, has expertise in the field of hydrometallurgical processes.

Redox system costs. - The system cost analysis carried out by UTC was for two separate system sizes and production levels specified by Lewis. The first was a 10-kW, 500-kWh system produced at a rate of 1000 per year. The second was a 10-MW, 100-MWh system with 100 being produced yearly. The former system was assumed to operate at a nominal 54 mW/cm^2, using one-molar reactants;

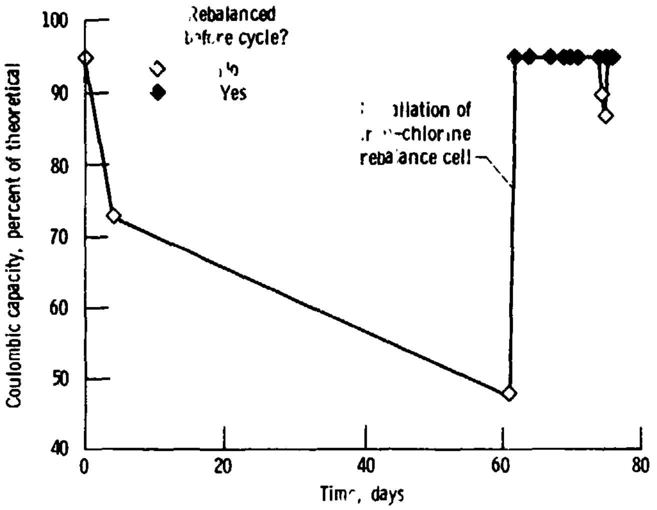


Figure 12. - Restoration of working cell capacity by use of iron-chlorine rebalance cell.

TABLE III. - TOTAL COSTS FOR PRODUCTION OF REDOX CHEMICALS

[Values in millions of 1981 dollars. Chromium, 22 700 metric tons per year, plus equivalent $FeCl_2$ and HCl.]

(a) Allied Chemical Company study

	Chlorination of prereduced chromite ore	Methanol reduction of sodium chromate	Electrolytic reduction of sodium chromate	Reductive chlorination of chromite ore
Total investment	$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	6.58	5.10	6.58	6.58
Fixed capital charges	10.10	10.80	17.10	40.00
Administrative expense	2.80	2.70	2.70	3.00
Return on investment (30 percent)	21.60	21.50	32.90	82.50
Total annual charges	$68.50	$85.16	$103.08	[a]$131.70
Total reactant cost:				
Per kg $CrCl_3$	$ 0.99	$ 1.23	$ 1.49	$ 1.91
Per kWh (unmixed reactants)	8.13	10.10	12.23	15.68

(b) Charles River Associates study

	From chromite ore	From ferrochrome	Reductive chlorination of chromite ore
Total investment	$69.34	$39.90	$95.33
Annual charges:			
Raw materials	$18.76	$36.70	$21.29
Energy	11.50	1.00	5.83
Labor and related	2.65	1.60	3.62
Fixed capital charges	10.42	4.70	14.44
Administrative expense	3.50	2.10	3.50
Return on investment (30 percent)	20.80	11.07	77.28
Total annual charges	$67.63	$58.07	$77.28
Total reactant cost			
Per kg $CrCl_3$	$ 0.98	$ 0.84	$ 1.12
Per kWh (unmixed reactants)	8.05	6.90	9.20

[a] Includes credit for sale of $MgCl_2$ and $AlCl_3$, $33 million.

the latter at 108 mW/cm^2, using two-molar reactants. In both cases the reactant cost was assumed to be about $22/kWh.

The results of the UTC study (ref. 31) indicate a system cost of $74/kWh for the 500-kWh system and $63/kWh for the 100-MWh system. These cost projections were encouraging. Although they were greater than the then-existing estimates for several competing technologies, they were much less than some of the more dire predictions; and they fell within the goals put forward for the major target applications.

For both system sizes the preponderant portion of the cost was associated with the reactants and their tankage. This amounted to 81 percent for the smaller system with its extended cycle length and 58 percent for the large, shorter-term system. Thus the results of the reactant cost studies were awaited with some anticipation.

<u>Redox reactant costs</u>. - Six processing routes for the [illegible]ction of the complete Redox system reactant package, which included acid [illegible] aqueous solutions of ferrous chloride and chromic chloride, were analyzed [illegible] the two contractors. All processes began with either chromite ore (Cr/Fe = 1.58 mass ratio), ferrochrome (Cr/Fe = 1.64), or the chemical intermediate, sodium chromate. For the sodium chromate starting material the necessary iron would be supplied to the process as scrap iron. 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 are therefore accepted as being quite accurate. These studies are presented in detail in references 32 and 33. The results of the two studies, adjusted to a common basis, are summarized in table III. The specific costs in dollars per kilowatt-hour assume an 80-percent utilization of reactants and an average cell discharge voltage of 0.9 V.

If the assumed reactant cost of $22/kWh, which was used in the UTC system cost analysis, is adjusted to the same basis, it becomes $16.50/kWh. This is roughly equal to the most expensive process evaluated by Allied and CRA. The remaining processes that were evaluated indicated reactant costs as low as about 45 percent of the most expensive. For example, the reactant cost for the methanol reduction of sodium chromate, a process evaluated and well understood by the Allied Chemical Co. is projected to be about $10/kWh. Since this is about $6/kWh less than the UTC assumption, it can be inferred that the total system costs would be closer to $57 to $68/kWh than $63 to $74/kWh.

The results of the system and reactant cost analyses served to lend further credibility to the ambient-temperature iron-chromium Redox storage system concept. To the attractive characteristics inherent in flow batteries and the proven technical viability of the system, economic viability had now been added - provided, of course, that the assumed performance levels were attainable.

Performance of Ambient-Temperature Iron-Chromium Redox System

In spite of all of the positive aspects of the ambient-temperature iron-chromium flow battery, as evidenced especially in the development and operation of the 1-kW system and in the various cost analyses, it yet failed to satisfy the perceived technical requirements of the marketplace. The problem was that satisfactory electrical/electrochemical performance of the individual working cells remained unproven. The difficulties resided in two specific technical areas: the membranes and the solution chemistry of the chromium reactant.

As discussed earlier, the targets for the critical membrane properties were a selectivity of 5 μg Fe/h cm^2 M and a resistivity of 1 ohm-cm^2. The best combination of properties actually achieved in given anion exchange membranes was a selectivity of 20 μg Fe/h cm^2 M and a resistivity of 2.6 ohm-cm^2. All developmental work indicated that there was very little prospect of a membrane technology breakthrough resulting in a significant improvement in either membrane characteristic that would not be accompanied by an unacceptable degradation in the other. Analytical studies (ref. 19) showed that the poor selectivities achieved would require some method of periodic reactant solution refurbishment in order to avoid complete reactant cross-mixing. This would, of course, introduce an operational expense that would at some point become unacceptable. The previously discussed osmotic solvent transfer through the membranes would also require some method of correction and increased operational cost. The same analytical studies also showed that the high membrane resistivities would either result in poor system voltage efficiencies or require operation at very low current densities, with attendant increases in cell stack costs. Thus the failure to achieve the desired membrane characteristics had a deleterious effect on the projections for both system cost and efficiency.

The difficulties encountered with the chromium reactant solution proved to be much more tractable. The existing problem was manifested during the cell charging process: the charge acceptance rates were poor and capacity utilization was low. An efficiency penalty was incurred as a result. A typical constant-voltage charging curve is shown in figure 13. It can be seen that the charge acceptance rate started to fall dramatically even at low states of charge. By the time the cell was half-charged, the acceptance rate was too low to be significant. A single cell, of course, eventually could be fully charged at these low rates, albeit with poor efficiency. For a multicell grouping, however, the acceptance rate soon would fall to a level that would just balance the loss mechanisms such as shunt currents. Effective charging would cease at that point, and as much as 50 percent of the theoretically available capacity would not be used.

These performance characteristics, plus observed hysteresis effects for both the open-circuit voltage and the chromium solution color as functions of state of charge (ref. 2), led eventually to the understanding that more than one chromic ion species was being encountered. Spectrophotometric methods were used (ref. 34) to verify that there were, in fact, two predominant chromic ion species, the hexaaquo chromium (III) and the monochloropentaaquo chromium (III), in equilibrium at room temperature. They were about equal in concentration and the equilibration rate between them was quite low. Most significantly, only one of these species, the monochloropentaaquo chromium (III), was electrochemically active. Thus the poor charging characteristics were understood to result from the depletion of the active chromic ion species early in the charging process. The hysteresis effects also resulted from this depletion.

The same spectrophotometric studies next revealed that an increase in the chromium solution temperature would shift the equilibrium to favor the active chromic ion species and also speed up the rate of equilibration. Figure 14

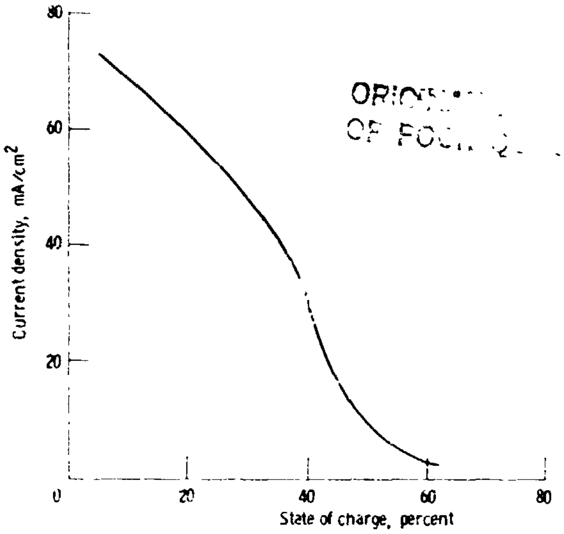


Figure 13. - Effect of state of charge on constant-voltage charge-acceptance rate. Charge, 1.3 V; temperature, 25 °C.

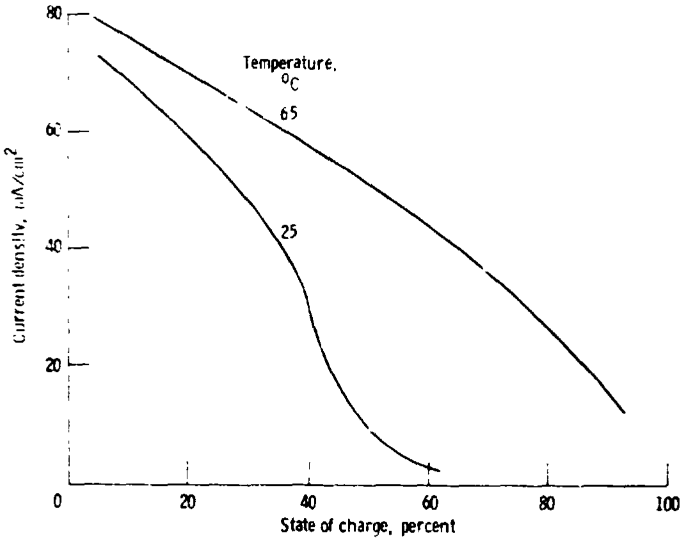


Figure 14. - Effect of chromium reactant equilibration temperature on constant-voltage charge-acceptance rate. Charge, 1.3 V.

TABLE IV. - EFFECT OF TEMPERATURE ON SELECTIVITY OF MEMBRANES DEVELOPED FOR AMBIENT-TEMPERATURE OPERATION WITH SEPARATE REACTANTS

Membrane	Temperature, °C			
	25°	45°	65°	80°
	Selectivity, μg Fe/h cm² M			
CDIL-AA5-LC (27.5 NP) (s [illegible] rd)	23.1	83.4	168	501
CDIL-A5-LC (20 NP)	5.5	42.4	96	212
Electrotechnical Laboratory (Japan) sample	77.0	184.3	293	659
RAI 1133-118-5	26.4	27.8	105	158

compares the constant-voltage charge acceptance rates of a cell having room temperature-equilibrated chromium reactant and a cell having chromium reactant equilibrated at elevated temperature. The dramatic superiority of the latter case is revealed in the ability to charge at high rates to nearly 100 percent state of charge. Subsequent in-cell tests (ref. 35) verified an additional advantage of elevated-temperature operation, a reduction in membrane and electrolyte resistivity. Also, from a systems standpoint, it is obvious that higher temperatures would greatly simplify the rejection of waste heat.

All of this experimental work overwhelmingly indicated that it was imperative to operate the iron-chromium Redox system at elevated temperature. The benefits were too great to do otherwise. However, there was a significant detriment - the selectivity of the anion exchange membranes being used or evaluated at that time became worse by factors of 4 to more than 10 (table IV) when the temperature was raised to 65° C. As stated earlier, the best anion exchange membrane available for the ambient-temperature Redox system, the CD1L, was only marginably acceptable in its ability to keep the reactant cations separate at 25° C. With this same membrane being used in cells at 65° C, complete cross-mixing of the reactants occurred rapidly. The likelihood of developing a new membrane with low resistivity and good selectivity for use at 65° C was much less even than that for 25° C operation. For these reasons the possibility of operating with mixed reactants at elevated temperature became the next focal point of development for the iron-chromium Redox storage system.

REDOX STORAGE SYSTEM AT ELEVATED TEMPERATURE

As was explained in the previous section, the equilibrium between active and inactive chromic ion species dictated that the iron-chromium flow battery be operated at about 65° C. Although this increase from the previous 25° C operating point solved the then-existing operational difficulties, it also introduced the possibility of problems with materials compatibility and corrosion. It was therefore necessary to reevaluate at 65° C the cells and cell components that had been developed for use at 25° C.

It soon became obvious that no state-of-the-art anion exchange membrane could provide adequate selectivity at the higher temperatures. Thus the near-perfect separation of the reactant metal cations, as called for by the classic flow battery concept, ceased to be a viable option. This fact lead to the realization that, for the iron-chromium battery to function acceptably at 65° C, it would have to be able to operate with reactants that had undergone complete cross-mixing.

Mixed-Reactant Mode of Operation

In this operating mode, both reactant solutions, when fully discharged, are identical. Typically they would be 1 M $FeCl_2$, 1 M $CrCl_3$, and 2 to 3 N HCl. The fully charged positive reactant stream would be 1 M $FeCl_3$, 1 M $CrCl_3$, and 2 to 3 N HCl. Similarly, the fully charged negative reactant stream would be 1 M $FeCl_2$, 1 M $CrCl_2$, and 2 to 3 N HCl.

Once this concept was considered, several potential advantages became apparent. For example, since selectivity would no longer be a significant criterion for membrane selection, it would be possible to stress low resistivity since the primary purpose of the membrane then would be merely to prevent convective (bulk) cross-mixing of the reactant streams. The new, low-resistance membranes would result in operation at high voltage efficiencies, but with the penalty of lower coulombic efficiency, because of increased diffusional self-discharge across the membrane. However, the loss of capacity due to this cross-diffusion, plus any osmotic solvent transfer, could be countered easily by occasionally discharging the system fully, reblending the two reactants, and then repartitioning them to their respective tankage systems. This, plus proper rebalancing to compensate for hydrogen evolution (or air intrusion), would make the system capacity virtually invariant. As shown in following sections, the actuality of these advantages and others for mixed-reactant operation has been verified.

In addition to the operational advantages perceived for the mixed-reactant, elevated-temperature mode of operation, several economic benefits were also anticipated: low membrane resistance would allow operation at high current densities, thus greatly reducing cell and stack size and therefore cost. Also, low-resistivity membranes with poorer selectivity would be expected to be much less expensive than their highly selective counterparts. On the other hand, the cost of reactants would be doubled for the mixed-reactant mode. Another negative aspect, mentioned earlier, is the reduction in coulombic efficiency. Open-circuit voltages would also be reduced at all states of charge by the thermodynamic effects of elevated temperature and reactant activity changes. These effects (fig. 15, ref. 36) resulted in a penalty of about 50 mV. Subsequent evaluation of the elevated-temperature, mixed-reactant operating mode has shown the advantages to considerably outweigh the disadvantages.

Electrodes

Because of the importance to system operation of proper chromium electrode performance, it was of immediate concern that the elevated temperature or the mixing of reactants might prove deleterious to the performance of the chromium electrode catalyst. Several evaluations were carried out in-house and at Giner, Inc., to examine these possibilities.

With regard to the mixing of reactants, per se, several tests were carried out at Giner, Inc. (ref. 14), using cyclic voltammetry. The effect of ferrous chloride ($FeCl_2$) on the electrochemical performance of a gold-catalyzed electrode in a chromic ion solution was first determined. The $FeCl_2$ concentration of the chromium solution was incrementally increased from 0 to 0.5 molar. The results (fig. 16) 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 because of 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 (fig. 17). 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.

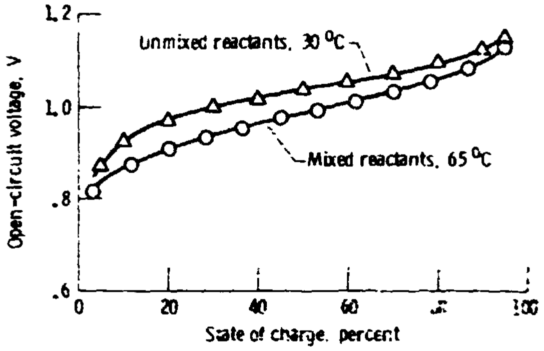


Figure 15. - Effect of state of charge on open-circuit voltage for two operating modes.

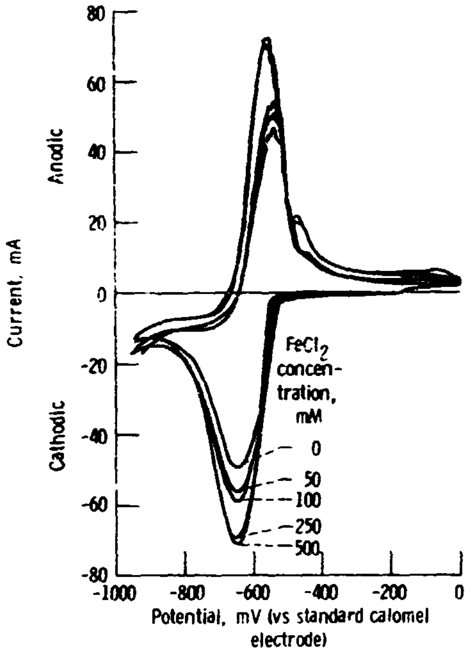


Figure 16. - Effect of FeCl$_2$ additions on chromium redox reactions. Gold-lead catalyst; [CrCl$_3$] = 50 mM; temperature, 25 °C.

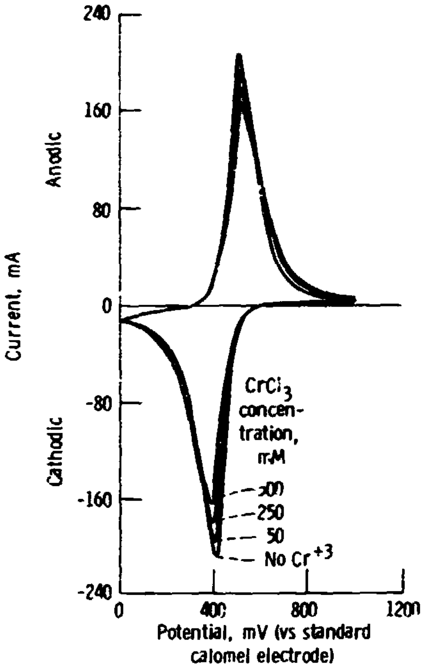


Figure 17. - Effect of CrCl$_3$ additions on iron redox reactions. [FeCl$_2$] = 50 mM; temperature, 25 °C.

How these results relate to actual working cell performance is unclear, especially in light of the fact that the concentration of the species being reduced and oxidized in each case was only 50 mM, while that of the "cross mixed" species was varied to 500 mM. Also these tests were carried out at 25° C. In any event, the observed effects are probably just a very small part of the overall thermodynamic effect of cross-mixing discussed earlier.

At Lewis the possible effect of temperature on electrode performance was investigated by using a standard laboratory cell containing an RAI anion exchange membrane and the gold-lead catalyst (ref. 19) with unmixed reactants. After 104 electrical cycles, which were accompanied by thermal cycling to 65° C, polarization tests indicated no loss of reversibility. During the testing of this cell there also was no increase in the rate of hydrogen evolution. However, the evolution rate was about 6 percent of the charge capacity, which was three or four times greater than normal for room-temperature operation. In general, the testing of several cells with the gold-lead catalyst revealed no loss of reversibility nor increase in hydrogen evolution rate during continued operation at elevated temperature. However, the hydrogen rate did vary considerably from cell to cell, ranging from a low of about 1 percent to the earlier mentioned 6 percent of charge capacity. This inconsistency was considered to be significant and led to the evaluation of other candidate catalysts for the chromium electrode.

The first question addressed was whether, at elevated temperature, any 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 (fig. 18) revealed irreversible behavior for both charge and discharge. Next a planar carbon surface was ion etched to increase its surface area. Tested 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 plate performed even more poorly. Adding bismuth and lead salts to the chromium reactant solution in order to suppress hydrogen evolution was beneficial, but the net improvement left much to be desired. Probably the attempt to deposit materials on this surface 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 led to the growth of an appreciable mass-transport boundary layer that inhibited 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 any deterioration 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 its current-voltage curves showed several steps during constant-load discharges.

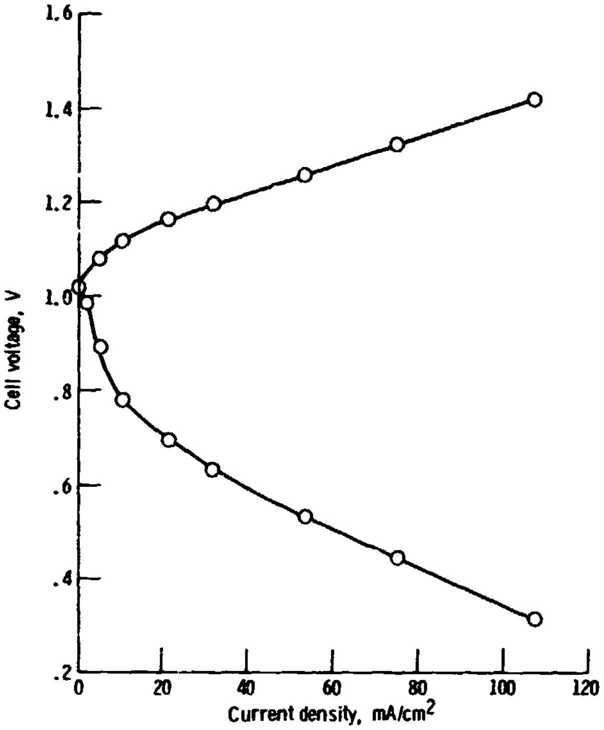


Figure 18. - Charge and discharge polarization curves for cell with lead-catalyzed chromium electrode. State of charge, 50 percent; temperature, 65 °C; unmixed reactants.

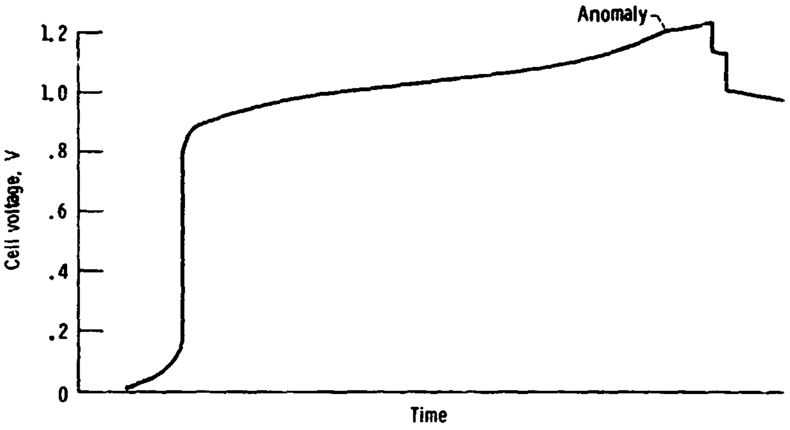


Figure 19. - Occasional charging anomaly, when using bismuth-lead catalyst for chromium electrode. Constant-current charge, 60 mA/cm^2; temperature, 65 °C; mixed reactants.

Another gold-lead analog, this time replacing the gold with bismuth, was selected for testing according to the same rationale as for silver-lead. Under certain test conditions this catalyst combination exhibited some unexplained performance anomalies (fig. 19). Typically at some point during a constant-current charge cycle an unexpected acceleration would occur in the rate at which the cell voltage was rising. This was indicated by the "blip" in the voltage-versus-time curve. The rate of voltage increase would then decline, and the voltage would approach more-or-less normal values near the completion of charge. The significant thing about this anomaly is, that if polarization data were taken at any time after such an excursion but before the stripping of the catalyst from the chromium electrode (i.e., before complete discharge), the cell performance would be irreversible. This irreversibility is indicated by the curvature in the polarization curves and by an apparent cell resistance greater than that indicated by an ac bridge (fig. 20). As the amount of bismuth salt in the chromium solution was increased relative to the amount of lead salt, the anomaly occurred at higher states of charge and its apparent magnitude became less. Nonetheless, no matter how small it was, if the anomaly was allowed to occur, irreversibility ensued. As mentioned earlier, the physics of these occurrences is not understood and has not been explored. It seems apparent, however, that for some reason a change occurs in the physical structure of the bismuth-lead catalyst combination that destroys its electrochemical activity.

In spite of the foregoing, the bismuth-lead catalyst behaved well as long as the state of charge of the working cell was not too high. Specifically performance was reversible and the hydrogen evolution rate was very low. Two cells that were identical except for the use of gold-lead in one case and bismuth-lead in the other were compared (fig. 21). The efficiencies of the two cells during 64.5-mA/cm^2 cycles were nearly identical, and the bismuth-lead hydrogen evolution rate was significantly lower.

Since it was the lead component of the bismuth-lead combination that seemed to cause the performance difficulties, and since bismuth is known to have an appreciable hydrogen overpotential of its own, bismuth next was evaluated alone as the chromium electrode catalyst. The performance of this material was excellent in virtually all respects and greatly enhanced the operational characteristics of the Redox system in the elevated-temperature, mixed-reactant mode of operation.

To date, the only known criteria that had to be satisfied for good performance with the bismuth catalyst were an operating temperature above 45° C (fig. 22) and a bismuth loading of about 35 µg/cm^2 of electrode area (fig. 23). Slightly more hydrogen did tend to be evolved from bismuth than from bismuth-lead, but the amount was still only about 1 percent of charge capacity, which is fully acceptable.

Several advantages are intrinsic to the bismuth catalyst when compared with gold-lead. These are related to the fact that the bismuth is soluble in the chromium reactant fluid when the reactant was fully discharged. Thus the bismuth catalyst surface is easily formed by electrodeposition, whereas gold required a cumbersome thermal deposition process preceded by extensive pretreatment of the carbon felt substrate. The bismuth solubility also resulted in a very "forgiving" catalyst system that can be fully restored, should any difficulty occur, simply by stripping and replating. This is in contrast to gold, which is very difficult to remove from its carbon felt substrate and

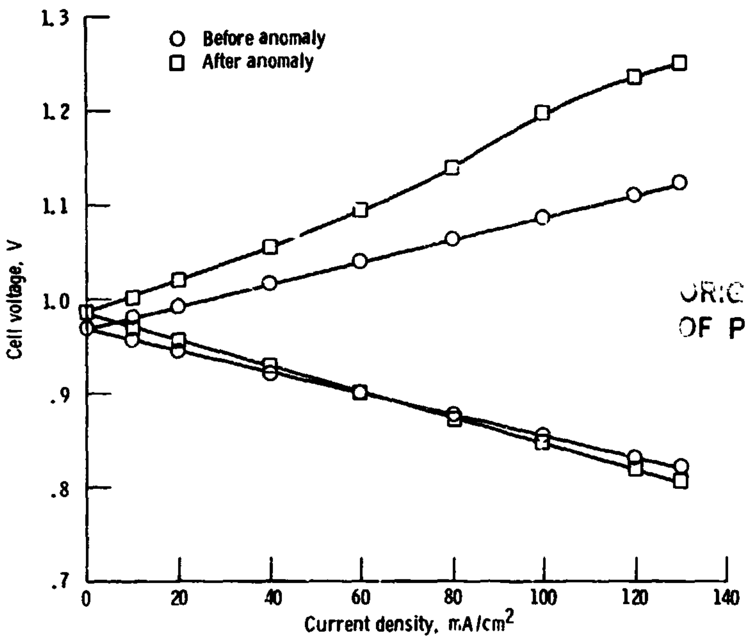
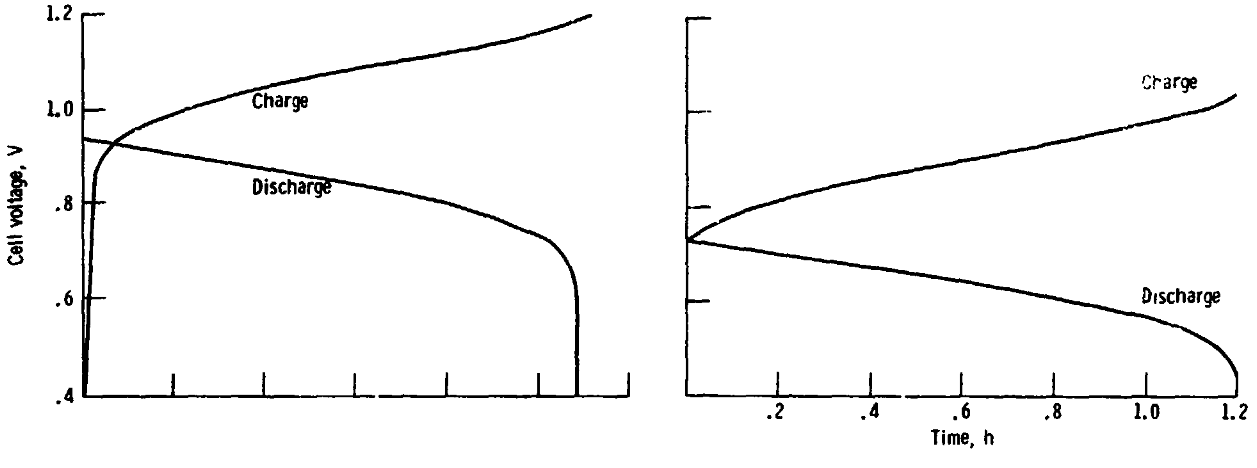


Figure 20. - Effect of charging anomaly on subsequent cell performance. Bismuth-lead catalyst; temperature, 65 °C; mixed reactants.



(a) Gold-lead chromium electrode catalyst; cell resistivity, 1.76 ohm-cm^2; membrane resistivity, 0.36 ohm-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.

(b) Bismuth-lead chromium electrode catalyst; cell resistivity, 1.74 ohm-cm^2; membrane resistivity, 0.34 ohm-cm^2; energy efficiency, 73.1 percent; coulumbic efficiency, 94.6 percent; voltage efficiency, 77.2 percent; hydrogen evolution, 0.2 percent of charge capacity.

Figure 21. - Cell voltage during constant-current cycle. State of charge, 0 to 87 percent; current density, 64.5 mA/cm^2; temperature, 65 °C; mixed reactants.

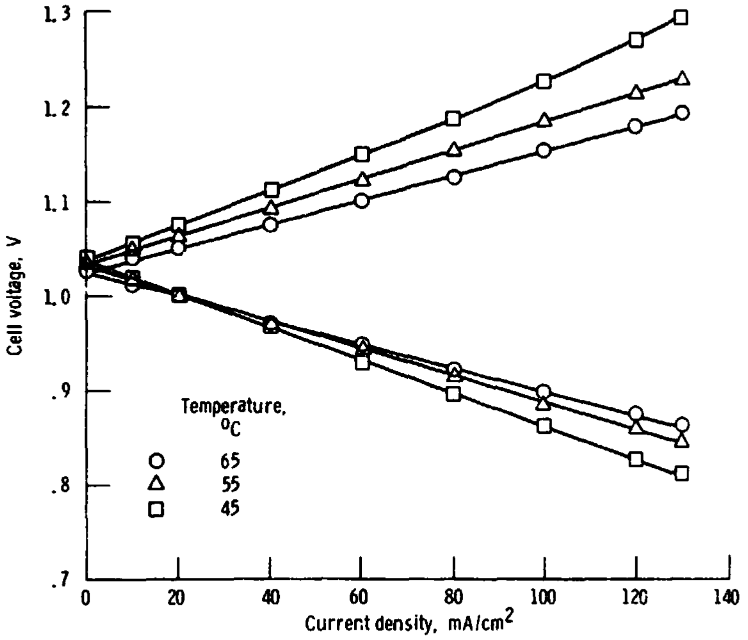


Figure 22. - Effect of operating temperature on charge and discharge performance. Bismuth chromium electrode catalyst; state of charge, 75 percent; mixed reactants.

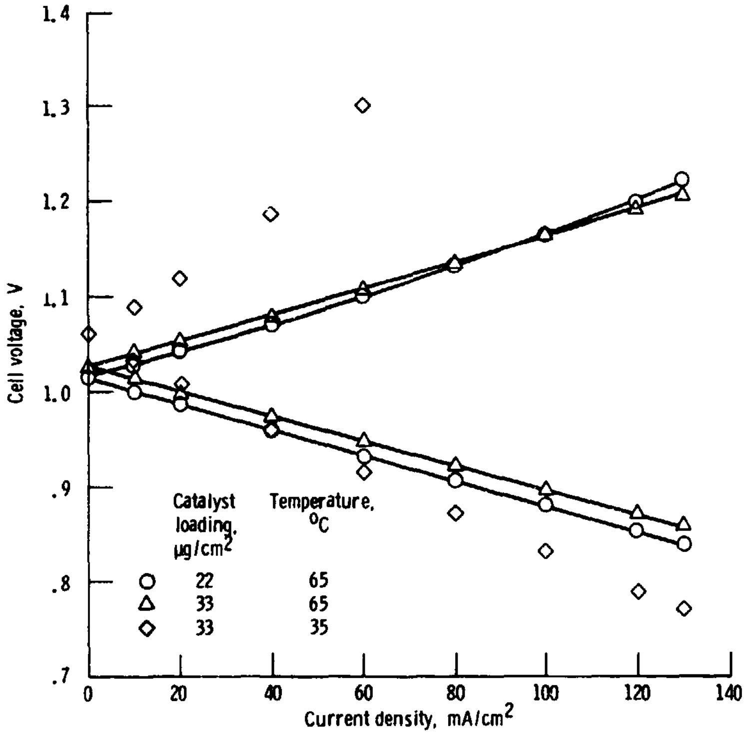


Figure 23. - Effect of catalyst loading and temperature on charge and discharge performance. Bismuth catalyst; state of charge, 75 percent; mixed reactants.

which, as discussed earlier, is susceptible to attack by oxidizing agents, with subsequent loss of reversibility or an increase in hydrogen evolution. No successful method for restoring the performance of a gold-catalyzed electrode was developed.

One unique characteristic of a Redox system operating with mixed reactants and a soluble catalyst such as bismuth is that the choice of which electrode is to be positive is entirely arbitrary. That is to say, if the proper amount of bismuth salt is added to both fully discharged reactants, the system is totally symmetrical and the respective half-cells, plus their associated reactants, are indistinguishable. This could be of advantage, for example, if over time there were a net partitioning of reactants by electrodialysis or a net solvent transfer by electro-osmosis. The system could be discharged and then placed back into operation with its polarity reversed, thus driving the transferred materials back toward their initial locations, yet not interfering with the system's function as a storage device. This mode of operation has been used routinely in the laboratory. Polarization data for a cell in its initial configuration and after two subsequent polarity reversals (fig. 24) show cell performance to be totally unaffected by this treatment.

The net result of the development effort for a chromium electrode catalyst for operation with mixed reactants at elevated temperature was the emergence of bismuth as the most attractive candidate, by far. The use of the bismuth catalyst was shown to result in a very forgiving system with a surprisingly broad range of operational flexibility.

Membranes

As mentioned earlier, the inability of the present generation of anion exchange membranes to retain acceptable selectivity at temperatures of approximately 65° C made necessary the switch to the mixed-reactant mode of Redox system operation. Table V presents selectivities at ambient and elevated temperatures for the ion-exchange membranes, both anion and cation, evaluated at Lewis. These selectivities should be viewed in the context of the original target value of 5 $\mu g\ Fe^{+3}/h\ cm^2\ M$ deemed necessary for electric utility applications using unmixed reactants.

Although initially both anion and cation exchange membranes were screened for use at 65° C, attention soon was focused on the cation types. The reasons for this shift in emphasis had to do with the membrane's stability of resistivity, ease of fabrication, physical durability, and cost. Developmental membranes for evaluation at Lewis were acquired from Ionics, Inc., and from RAI Research Corporation. Several others were provided by the Electrotechnical Laboratories of Japan.

The primary criterion used to define the new membrane development goals was that the resistivity should be less than 0.5 ohm-cm^2. It was acknowledged, of course, that the greater the success in achieving this goal, the poorer would be the membrane selectivity and the greater would be the resulting cell self-discharge rate. Therefore there exists, for a given membrane, an optimum current density that will maximize the cell energy efficiency. The effect of current density on working cell coulombic and energy efficiency for the membranes evaluated at Lewis is shown in figure 25. A change in current density can be pictured as occurring in either of two ways: a change in current for a

TABLE V. - EFFECT OF TEMPERATURE ON SELECTIVITY OF MEMBRANES FOR ELEVATED-TEMPERATURE OPERATION WITH MIXED REACTANTS

Membrane	Type	Source	Temperature, °C	
			23	65
			Selectivity, μg Fe/h cm² M	
W285-68E	Anion	Ionics	130	370
W285-64A	Cation		1130	1270
W285-64C			960	1270
W285-9039			1730	3670
W285-87			400	850
W285-89			210	650
W285-99 (7 mil)			1435	2890
W285-99 (4 mil)			2210	3775
MT306-34			255	615
CPS-1			----	8060
MT281-89			35	167
CMV		Asahi	60	210
1155-214-135		RAI	770	1060
1155-214-90			1360	1930
1155-214-45			2450	3140
1155-213-45			590	850
1155-213-90			400	570
1155-213-135			260	345
ML-21			1105	2350

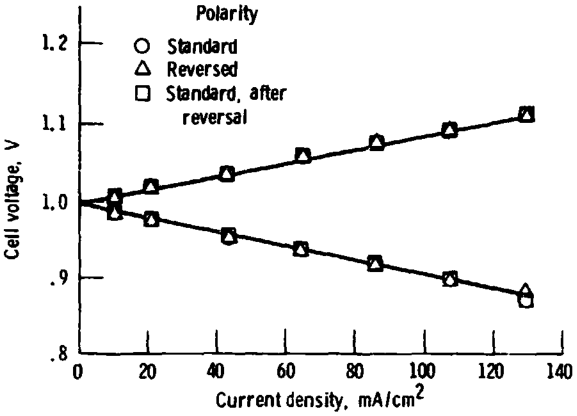
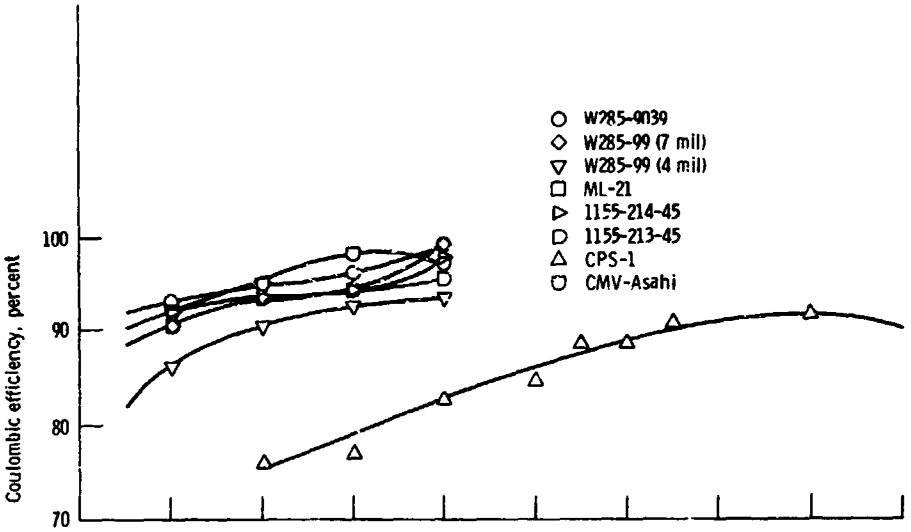
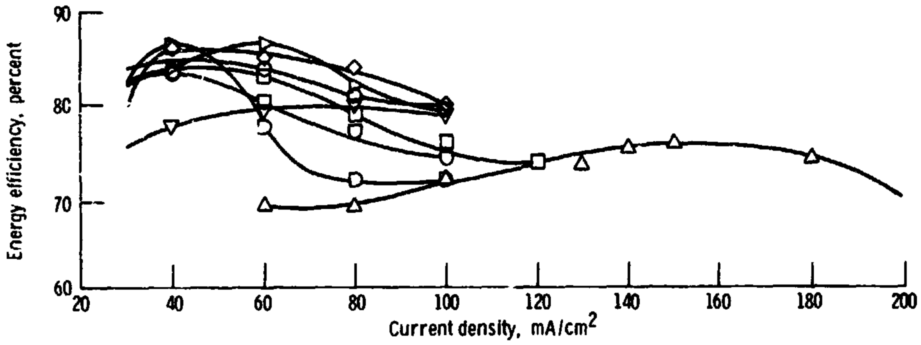


Figure 24. - Effect of complete polarity reversal on performance. Bismuth catalyst; ML-21 membrane; state of charge, 50 percent; temperature, 65 °C; mixed reactants; bismuth salt in each reactant.



(a) Coulombic efficiency.



(b) Energy efficiency.

Figure 25. - Effect of current density on working cell efficiency for developmental membranes. Constant-current cycles; temperature, 65 °C; mixed reactants.

cell of fixed size (the normal laboratory procedure), or a change in cell size for a fixed current (as in the redesign of a system). In either case, increasing current density will reduce the voltage efficiency. But the coulombic efficiency will improve because of the shorter cycle or the reduced membrane area, depending on how the current density increase was implemented.

The precise relationship between resistivity and selectivity for a given membrane type cannot be predicted, beyond the fact that it is an inverse function. Nor can either of the two characteristics be varied independently of the other. Thus the membrane evaluation task at Lewis evolved into the process of obtaining new membranes offering a wide range of resistivity/selectivity combinations and operating them in working cells. Resistivity is plotted against selectivity in figure 26 for the membranes tested at Lewis. Each membrane was evaluated at elevated temperature, using mixed reactants. Constant-current cycles were carried out between fixed cutoff voltages (ref. 37). For each membrane the coulombic and energy efficiencies typically were determined for such cycles over the current density range 40 to 120 mA/cm^2, depending on where the peak energy efficiency occurred. Table VI presents a typical set of data for one of the developmental membranes. This mapping process resulted in a data base presenting, at least implicitly, the relationships between resistivity, selectivity, current density, and cell operating efficiency for each of the developmental membranes. Table VII summarizes these data, showing for each membrane the resistivity, selectivity, and performance characteristics at its optimum current density.

The most significant aspect of these data, of course, is that excellent energy efficiencies were obtained at current densities much greater than usual for flow battery operation, which is about 30 mA/cm^2. The associated high power densities (in milliwatts per square centimeter) will result in much smaller, and therefore less expensive, cells and stacks than previously required for a given system power level. The data also indicate that membranes might be selected for their suitability for particular applications (ref. 1). For example, if a storage system must be used in a standby mode for extended periods, a membrane offering good coulombic efficiency might be preferable to one capable of high-rate operation. On the other hand, applications that place a premium on capital cost might require the smallest possible cells and stacks.

The cycling of Redox cells at high current densities between fixed cutoff voltages raises the question of the effect of current density on reactant utilization For example, for a cell being discharged, the greater the current density, the higher will be the state of charge when the cutoff voltage is reached. Computations were done using a model based on current density, cell resistivity, cutoff voltages, and reactant flow rates. The results (table VIII) indicate that even at current densities of 100 mA/cm^2, a cell of 0.8-ohm-cm^2 resistivity would operate between state-of-charge limits of 4.7 and 95.3 percent, giving a reactant utilization of 90.6 percent. Normal operation of a Redox system typically is assumed to be between 10- and 90-percent state of charge, giving a utilization of 80 percent. Thus operation even at high current densities will not have a significant effect on reactant utilization.

The transport processes occurring across a charged membrane in the presence of ionic species and potential gradients are complex (ref. 12). As mentioned earlier, there usually is a net amount of solvent transfer from one reactant system to the other. There also will be a partitioning of the

ORIGINAL PAGE IS
OF POOR QUALITY

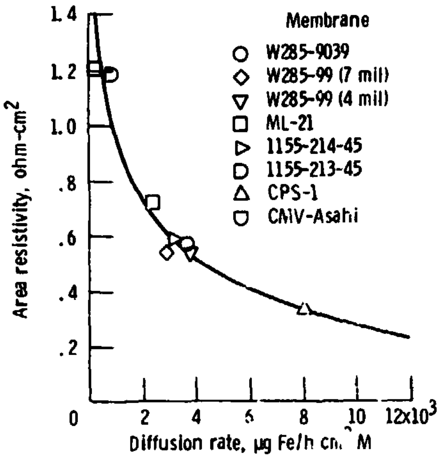


Figure 26. - Experimental correlation of selectivity and resistivity for developmental membranes.

TABLE VI. - EFFECT OF CURRENT DENSITY ON REDOX CELL EFFICIENCY

[Ionics W285-99 (7 mil) membrane; temperature, 65° C, mixed reactants.]

Current density, mA/cm²	Energy efficiency, percent	Coulombic efficiency, percent	Membrane resistivity, ohm-cm²
30	79	88	0.55
40	84	90	.53
60	85	93	.53
80	81	94	.64
100	79	99	.55

TABLE VII. - REDOX CELL PERFORMANCE FOR VARIOUS MEMBRANES AT THEIR RESPECTIVE OPTIMUM CURRENT DENSITIES

[14.5-cm² cell; temperature, 65° C; mixed reactants.]

Membrane	Source	Optimum current, density, mA/cm²	Membrane resistivity, ohm-cm²	Coulombic efficiency, percent	Energy efficiency, percent	Selectivity, µg Fe/hr cm² M
OMV-Asahi	Asashi	40	1.21	92	8[illegible]	210
ML-21	RAI	↓	.72	92	86	2000
W285-9039	Ionics	↓	.49	93	86	3700
1155-213-45	RAI	↓	1.19	92	87	850
W285-99 (7 mil)	Ionics	60	.53	93	85	2900
1155-214-45	RAI	60	.59	93	87	3100
W285-99 (4 mil)	Ionics	80	.53	93	80	3800
CPS-1	Ionics	150	.33	91	76	8059

TABLE VIII. - EFFECT OF CURRENT DENSITY ON REACTANT UTILIZATION FOR CONSTANT-CURRENT CYCLES BETWEEN CUTOFF VOLTAGES OF 1.20 V and 0.76 V

[Cell resistivity, 0.8 ohm-cm²; reactant flow rate, 1.5 times stoichiometric.]

Current density, mA/cm²	State of charge, percent		Reactant utilization, percent
	Maximum	Minimum	
40	97.8	2.2	95.6
60	97.2	2.9	94.3
80	96.3	3.6	92.7
100	95.3	4.7	90.6

reactants depending on, among other factors, the diffusivities of the various reactant ion species.

For operation in the unmixed-reactant mode these transport processes threaten severe reactant maintenance difficulties, especially over long durations. In the mixed-reactant mode, however, they are easily accommodated. Either on a scheduled basis or in response to the exceeding of an established limit, the cell or system can be fully discharged and the two reactant volumes completely mixed. If the reactants have been kept chemically in balance, and if both contain adequate bismuth salt, the redistribution of equal reactant volumes to the respective tankage systems after reblending will completely reverse the effects of any net reactant or solvent transport. This process was carried out many times in the laboratory and became a routine part of th normal operation of cells. Figure 27 includes polarization data taken before and after a period of cycling during which the reactants were reblended three times. The polarization curves are unchanged, showing that this treatment, which is made necessary by the membrane characteristics, has no adverse effect on the activity of either cell electrode.

The development effort for membranes specifically for use in Redox cells operating at 65° C with mixed reactants thus has had considerable success. A series of cation exchange membranes with low resistivities have been developed by two primary suppliers, Ionics, Inc., and the RAI Research Corporation, and evaluated at Lewis. Cells using these membranes have been shown to operate at high efficiency, even at current densities approaching 100 mA/cm^2. The membranes are sturdy and showed no deterioration while being tested. However, test durations were short, none exceeding 4 months; life testing would be an important requirement for any further development effort.

Performance and Cost

The improvement in Redox cell performance that has resulted from the change to operation with mixed reactants at 65° C is illustrated in Table IX. A comparison is made between a cell operating in the new mode and a cell at 25° C with unmixed reactants. Each cell is shown to be operating at a current density typical for its respective operating mode; each cell is assumed to be in a bipolar stack so that total cell resistivity is nearly equal to the membrane resistivity.

The most significant difference between the cells is, of course, the fivefold reduction in membrane resistivity for the new operating mode. This in turn results in an increase in power density, from 29 to 73 mW/cm^2, with virtually no loss in energy efficiency.

For the new operating mode the effect of the higher temperature on the equilibrium between chromic ion species permits full reactant utilization, compared with 40 to 50 percent for the 25° C system. In the light of this characteristic, the argument could be made that, in order for the two systems to have equal capacity, the 25° C system would require a 100 percent excess of chromium reactant to allow for the fraction of chromic chloride that was electrochemically inert. Thus the apparent cost penalty for operation with mixed reactants would become insignificant. Even disregarding this argument, though, it still seems unlikely that the cost of reactants per kilowatt-hour of mixed-reactant

ORIGINAL PAGE IS
OF POOR QUALITY

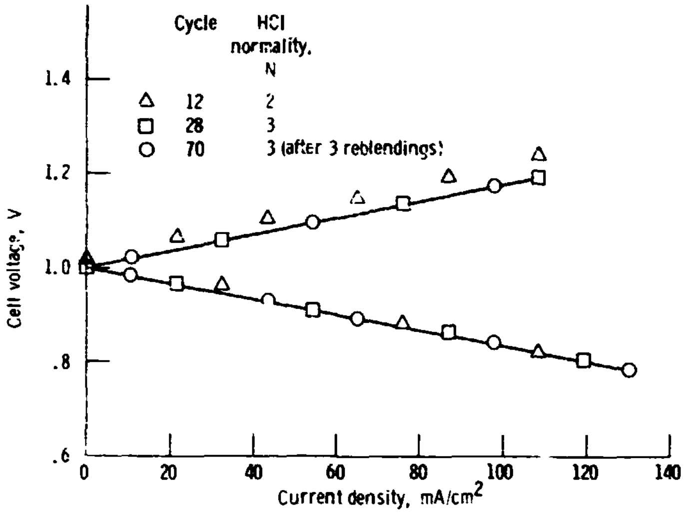


Figure 27. - Redox cell polarization performance during extended cycling, including three reblendings of reactants. Bismuth-lead catalyst; ML-21 membrane; state of charge, 50 percent; temperature, 65 °C; mixed reactants.

TABLE IX. - COMPARISON OF REDOX SYSTEM OPERATING MODES

	Unmixed reactants at 25° C	Mixed reactants at 65° C
Membrane resistivity, ohm-cm^2	2.5	0.5
Selectivity, μg Fe/h cm^2 M	20-30	3000
Open-circuit voltage at 50-percent state of charge, V	1.05	0.95
Nominal current density, mA/cm^2	30	80
Nominal power density, mW/cm^2	29	73
Cell efficiency, percent:		
Voltage	87	92
Coulombic	99	95
Energy	86	87
Capacity utilization, percent	40	90

operation would be twice that for operation with separate reactants. The reason is that the expensive separation of iron and chromium salts, necessary for the production processes starting with chromite ore or ferrochrome, could be eliminated.

As discussed earlier, the system cost study by UTC indicated that a system operating at 108 mW/cm^2, with separate reactants at $22/kWh and tankage at $0.60/gal, would cost about $63/kWh. On the basis of the reactant cost studies by the Allied Chemical Co. and CRA, a cost of $20/kWh for mixed reactants does not seem unreasonable. By making a correction per the previous table, for operation at 73 mW/cm^2, a total system cost for mixed-reactant operation of $65/kWh to $75/kWh can be derived from the UTC analysis, depending on the assumptions concerning tankage cost. (The higher figure corresponds to the UTC assumption.)

It thus appears that the Redox cell performance improvements associated with operation at 65° C with mixed reactants are nearly "free." That is to say, there is no obvious cost penalty that would militate against the use of this operating mode.

CONCLUDING REMARKS

The completion of the Redox project finds the state of iron-chromium flow battery technology to be quite encouraging. During the earlier phases of the project, and in spite of relatively poor electrochemical performance at that time, the basic concept of the Redox battery was shown to be technically viable. This was particularly true for the system-level functions such as rebalancing, determining the state of charge, and using trim cells. These functions, plus the remarkable operational flexibility of the Redox system were demonstrated during the testing of a 1-kW, 13-kWh system used as storage for a photovoltaic array. Also, with regard to single-cell development, there were several very significant accomplishments. Probably the most notable of these was the development of the gold-lead catalyst for chromium electrode reactions. For the first time it became possible to obtain good redox reaction kinetics while minimizing hydrogen evolution. New classes of anion exchange membranes also were developed. Although not achieving the existing target values for resistivity and selectivity, these membranes were "fine tuned" until they offered the best tradeoff between these two characteristics available among the present generation of membranes.

The long-sought-after breakthrough in electrochemical performance came through the realization that the chromium reactant contained a chromic ion species that was electrochemically nonreactive. This revealed the need to increase the operating temperature from 25° to 65° C, which in turn made necessary operation with mixed reactants. The new mode of operation permitted the use of membranes that, although having very poor selectivities, had the advantage of very low resistivities, around 0.5 ohm-cm^2. These changes in the design and mode of operation of Redox cells increased the operating current density from 20 to 30 mA/cm^2 to 60 to 80 mA/cm^2 without an attendant loss of efficiency.

A new chromium electrode catalyst, bismuth, was developed for operation at elevated temperature. This catalyst is active for the chromium redox reactions yet has a high hydrogen overpotential. In addition, it is easily stripped and reformed, which makes possible a very "forgiving" system, capable of maintaining original levels of performance. Using this catalyst also increases the inherent flexibility of the Redox system.

Cost analyses for the 25° C, separate-reactant mode of operation indicated a selling price for mass-produced Redox systems of $60 to $70/kWh. Preliminary analysis for the 65° C, mixed-reactant mode suggested that the increased reactant cost essentially is balanced by the ability to use smaller stacks and less expensive materials. Thus the cost projections still show the Redox system to be capable of meeting the goals established by most potential users.

During the relatively brief development period for the 65° C, mixed-reactant operating mode (about 2 yr), no life-limiting characteristics were discovered. However, any future renewal of work on the iron-chromium system should include extended, methodical cycle life testing. Other than that, the Redox system is now considered to be ready for scaleup to a size adequate to evaluate its true potential for the commercial market for energy storage. Standard Oil of Ohio (Sohio) has undertaken such an evaluation of the technology, to be followed by further development, if warranted, and subsequent commercialization. The transfer of the technology to Sohio is supported by the NASA Technology Utilization Office, and an exclusive license for patents owned by NASA was obtained from NASA by Sohio.

REFERENCES

1. Hagedorn, Norman H.; and Thaller, Lawrence H.: Design Flexibility of Redox Flow Systems. Proceedings of the Seventeenth Intersociety Energy Conversion Engineering Conference, Vol. 2, IEEE, 1982, pp. 600-609.

2. NASA Redox Storage System Development Project - Calendar Year 1981. DOE/NASA/12726-19, NASA TM-83087, 1983.

3. Stalnaker, Dale K.; and Acevedo, Julio C.: An Electrochemical Rebalance Cell for Redox Systems. DOE/NASA/12726-20. NASA TM-83363, 1983.

4. Prokopius, Paul R.: Model for Calculating Electrolytic Shunt Path Losses in Large Electrochemical Energy Conversion Systems. NASA TM X-3359, 1976.

5. Stalnaker, Dale K.; and Lieberman, Arthur: Design and Assembly Considerations for Redox Cells and Stacks. DOE/NASA/12726-10, NASA TM-82672, 1981.

6. Hoberecht, Mark A.: Pumping Power Considerations in the Designs of NASA Redox Flow Cells. DOE/NASA/12726-7, NASA TM-82596, 1981.

7. Hagedorn, Norman H.; Hoberecht, Mark A.; and Thaller, Lawrence H.: NASA Redox Cell Stack Shunt Current, Pumping Power, and Cell Performance Tradeoffs. DOE/NASA/12726-11, NASA TM-82686, 1982.

8. Hoberecht, Mark A.; and Thaller, Lawrence H.: Performance Mapping Studies in Redox Flow Cells. DOE/NASA/12726-13, NASA TM-82707, 1981.

9. Thaller, L. H.: Electrically Rechargeable Redox Flow Cell. U.S. Patent 3,996,064, Dec. 1976.

10. Thaller, Lawrence H.: Electrochemically Rechargeable Redox Flow Cells. Ninth Intersociety Energy Conversion Engineering Conference, American Society of Mechanical Engineers, 1974, pp. 924-928.

11. Giner, J.; Swette, L.; and Cahill, K.: Screening of Redox Couples and Electrode Materials. NASA CR-134705, 1976.

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

13. Jalan, Vinod,; Morriseau, Brian; and Swette, Lawrence: Optimization and Fabrication of Porous Carbon Electrodes for Fe/Cr Redox Flow Cells. DOE/NASA.0198-1, NASA CR-167921, 1982.

14. Swette, L.; and Vinod, J.: Development of Electrodes for the NASA Iron/Chromium Redox System and Factors Affecting Their Performance. DOE/NASA/0262-1, NASA CR-174724, 1984.

15. Jalan, Vinod; Stark, Herbert; and Giner, Jose: Requirements of Optimization of Electrodes and Electrolyte for the Iron/Chromium Redox Flow Cell. DOE/NASA/009780/1, NASA CR-165218, 1981.

16. Reid, Margaret A., et al.: Preparation and Characterization of Electrodes for the NASA Redox Storage System. DOE/NASA/12726-13, NASA TM-82702, 1980.

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

18. Giner, J.; and Cahill, K.: Advanced Screening of Electrode Couples. DOE/NASA/0794-80/1, NASA CR-159738, 1980.

19. NASA Redox Storage System Development Project - Calendar Year 1982. DOE/NASA/12726-23, NASA TM-83469, 1983.

20. Redox Flow Cell Development and Demonstration Project - Calendar Year 1976. CONS/1002-3, NASA TM-73873, 1977.

21. Redox Flow Cell Development and Demonstration Project - Calendar Year 1977. DOE/NASA/1002-78/2, NASA TM-79067, 1979.

22. Alexander, Samuel; Geoffrey, Richard; and Hodgdon, Russell: Anion Selective Membrane. NASA CR-134931, 1975.

23. Alexander, S. S.; and Hodgdon, R.: Anion Permselective Membrane. NASA CR-135316, 1978.

24. Alexander, Samuel S.; Hodgdon, Russell; and Waite, Warren A.: Anion Permselective Membrane. DOE/NASA/0001-79/1, NASA CR-159599, 1979.

25. Hodgdon, Russell; and Waite, Warren A.: Anion Permselective Membrane. DOE/NASA/0137-1, NASA CR-165223, 1980.

26. Hodgdon, Russell; and Waite, Warren A.: Anion Permselective Membrane. DOE/NASA/0204-1, NASA CR-167872, 1982.

27. O'Donnell, Patricia M.; Sheibley, Dean W.; and Gahn R.: Anion Exchange Membrane for Electrochemical Oxidation-Reduction Energy Storage System. ERDA/NASA/1002-77/2, NASA TM-73751, 1977.

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

29. Thaller, L.: Recent Advances in Redox Flow Cell Storage Systems. Proceedings of the Fourteenth Intersociety Energy Conversion Engineering Conference, American Chemical Society, 1979, pp. 715-719.

30. Hagedorn, Norman H.: NASA Preprototype Redox Storage System for a Photovoltaic Stand-Alone System. Proceedings of the Sixteenth Intersociety Energy Conversion Engineering Conference, American Society of Mechanical Engineers, 1981, pp. 805-811.

31. Michael, Kenneth; and Hall, Gene: Cost Projection for Redox Energy Storage Systems. (FRC-1784, United Technologies Corp; NASA Contract DEN3-126.) DOE/NASA/0126-1, NASA CR-165260, 1980.

32. Ammann, Paul; Loreth, Michael; and Harvey, W. W.: Study to Establish Cost Predictions for the Production of Redox Chemicals. (CRA-605, Charles River Associates; NASA Contract DEN3-251.) DOE/NASA/0251-1, NASA CR-167882, 1982.

33. Walther, J. F., et al.: Study to Establish Cost Projections for Production of Redox Chemicals. DOE/NASA/0250-1, NASA CR-167881, 1982.

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

35. Gahn, R. E.; Johnson, J. A.; and Ling, J. S.: Single Cell Testing of the NASA Fe/Cr Redox System at Elevated Temperature. Extended Abstracts, Vol. 82-2, Electrochemical Society, 1982, pp. 407-408.

36. Gahn, Randall; Hagedorn, Norman; and Ling, Jerri S.: Single Cell Performance Studies on the Fe/Cr Redox Energy Storage System Using Mixed Reactant Solutions at Elevated Temperature. Proceedings of the Eighteenth Intersociety Energy Conversion Engineering Conference, American Institute of Chemical Engineers, 1983, pp. 1647-1652.

37. Ling, J. S.: Evaluation of Developmental Membranes for the Iron Chromium Redox System. Prepared for the 166th Meeting of the Electrochemical Society, New Orleans, LA, Oct. 7-12, 1984.