

DOE/NASA/1002-79/3  
NASA TM-79143

(NASA-TM-79143) REDOX FLOW CELL ENERGY  
STORAGE SYSTEMS (NASA) 11 P HC A02/MF A01  
CSCI 10A

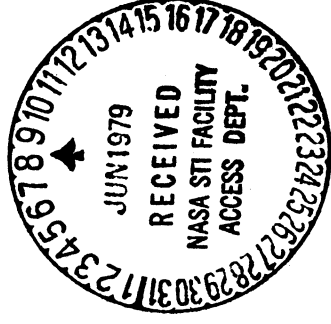
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# REDOX FLOW CELL ENERGY STORAGE SYSTEMS

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Work performed for  
**U.S. DEPARTMENT OF ENERGY**  
**Office of Energy Technology**  
**Division of Energy Storage Systems**



Prepared for  
Terrestrial Energy Systems Conference Sponsored by the  
American Institute of Aeronautics and Astronautics  
Orlando, Florida, June 4-6, 1979

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1. Report No. <b>NASA TM-79143</b>	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle <b>REDOX FLOW CELL ENERGY STORAGE SYSTEMS</b>		5. Report Date
		6. Performing Organization Code
7. Author(s) <b>Lawrence H. Thaller</b>		8. Performing Organization Report No. <b>E-9996</b>
		10. Work Unit No.
9. Performing Organization Name and Address <b>National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135</b>		11. Contract or Grant No.
12. Sponsoring Agency Name and Address <b>U. S. Department of Energy Division of Energy Storage Systems Washington, D. C. 20545</b>		13. Type of Report and Period Covered <b>Technical Memorandum</b>
		14. Sponsoring Agency <del>Code</del> Report No. <b>DOE/NASA/1002-79/3</b>
15. Supplementary Notes <b>Prepared under Interagency Agreement E(49-28)-1002. Presented at the Terrestrial Energy Systems Conference sponsored by the American Institute of Aeronautics and Astronautics, Orlando, Florida, June 4-6, 1979.</b>		
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17. Key Words (Suggested by Author(s)) <b>Energy storage Redox Batteries</b>	18. Distribution Statement <b>Unclassified - unlimited STAR Category 44 DOE Category UC-94c</b>	
19. Security Classif. (of this report) <b>Unclassified</b>	20. Security Classif. (of this page) <b>Unclassified</b>	21. No. of Pages 22. Price*



DOE/NASA/1002-79/3  
NASA TM-79143

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## REDOX FLOW CELL ENERGY STORAGE SYSTEMS

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Abstract

NASA-Redox energy storage systems are being developed for ultimate use in stand-alone village power applications and distributed energy storage installations for electric utility service. In the former application, either solar photovoltaic arrays or wind turbines supply the primary power and an electrochemical storage system stores energy during times of excess power generation capability and delivers energy during times of insufficient power generation. Electric utilities conceive of distributed energy storage for use either on a daily or weekly cycle to provide a load leveling capability for their large central station plants. Various electrochemical and non-electrochemical storage concepts are under consideration for these applications. Life cycle costs, simplicity of operation, complexity and state of technology are all determining factors in selecting systems for these important storage applications. NASA-Redox systems are electrochemical storage devices that use two fully soluble Redox couples, anode and cathode fluids, as active electrode materials separated by a highly selective ion exchange membrane. The reactants are contained in large storage tanks and pumped through a stack of Redox flow cells where the electrochemical reactions (reduction and oxidation) take place at porous carbon felt electrodes. A string or stack of these power producing cells is connected in series in a bipolar manner. Redox energy storage systems promise to be inexpensive and possess many features that provide for flexible design, long life, high reliability and minimal operation and maintenance costs. These features include independent sizing of power and storage capacity requirements and inclusion within the cell stack of a cell that monitors the state of charge of the system as a whole, and a rebalance cell which permits continuous correction to be made for minor side reactions that would tend to result in the anode fluid and cathode fluids becoming electrochemically out of balance. These system features will be described and discussed.

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Introduction

The need for storage has been identified as a firm requirement for remote power system applications that are supplied either by solar photovoltaic arrays or wind turbine generators.<sup>(1)</sup> Currently, lead-acid batteries can be used for this application but they are expensive and not easy to maintain at the system level.<sup>(2)</sup> Over the past six years, the NASA-Lewis Research Center has developed the NASA-Redox concept<sup>(3)(4)</sup> from the original idea (US Patent No. 3,996,064) to where small but complete Redox energy storage systems have been built. These systems promise to be very inexpensive systems constructed using relatively unsophisticated technologies. As with other electrochemical energy storage systems, energy is stored during periods when ample power is being produced by either the connected solar array or the wind turbine, and supplied to the various loads during periods of low production. In the remote village power system application, low life cycle cost and simplicity of operation are the major requirements. The power level of one of these systems would probably be low (tens of kilowatts), but the duration over which this power might have to be supplied is rather long (30 to 50 hours). An artist's rendition of a NASA-Redox installation is shown in Figure 1. A Redox energy storage system is seen to consist of two tanks, two pumps, a stack of Redox flow cells and associated controls.

Another application for energy storage systems is in electric utility service where they would serve in a load leveling capacity.<sup>(5)</sup> When distributed at the interface between the transmission network and the distribution lines, these storage devices (Figure 2) would reasonably be in the ten megawatt size range and used on a daily cycle (~8 hr. charge - 5 hr. discharge). However, for certain industrial applications, a weekly cycle appears attractive if the storage cost is low enough. Here also, the many attractive features of NASA-Redox energy storage systems make it an attractive candidate for this service.

The NASA-Redox Energy Storage System

Basically, the NASA-Redox system is an electrochemical storage device that utilizes the oxidation and reduction of two fully soluble Redox couples for charging and discharging. The Redox couples currently under investigation are acidified chloride solutions of chromium ( $\text{Cr}^{+2}/\text{Cr}^{+3}$ ) and iron ( $\text{Fe}^{+2}/\text{Fe}^{+3}$ ). Figure 3 illus-

trates the system in its simplest form. This shows that the reactant solutions are stored in tanks outside the power conversion section in which the associated electrochemical reactions take place at inert electrodes. The Redox solutions that are pumped through the porous electrodes and kept separated by a highly selective ion exchange membrane that has been developed for this application under a series of contracts by Ionics Incorporated of Watertown, Massachusetts. This membrane has been engineered to almost completely prohibit the passage of iron and chromium ions and yet allow easy passage of chloride and hydrogen ions. The reactant solutions are currently 1.0 molar in either iron or chromium chloride and 2.0 normal in hydrochloric acid. The inert electrodes are highly porous carbon felt material manufactured by Fiber Materials Incorporated of Biddeford, Maine. The electrode material used on the chromium side of the cell is catalyzed with small amounts of lead and gold. This catalyst system was developed under contract by Giner Incorporated of Waltham, Massachusetts as part of the overall Redox technology effort. (7) Techniques were subsequently developed at the Lewis Research Center to apply this catalyst system to large area carbon felts used as the electrode material in cells tested in our laboratory. The electrochemical reactions are very simple (Figure 3) and highly reversible. When the system is in the charged state, the chromium solution is mostly chromous ion and the iron solution, ferric ion. As the fluids are pumped through the system and they undergo discharge, the chromous ions are oxidized to chromic ions and the ferric ions are reduced to ferrous ions. To maintain overall charge neutrality in the system, these electrochemical reactions are accompanied by the gain of chloride ion (and/or loss of hydrogen ion) in the chromium solution and the commensurate loss of chloride ion (and/or gain of hydrogen ion) in the iron solution. The discharge processes may be summarized as follows:

At anode:  $\text{Cr}^{+2} + \text{Cr}^{+3} + \text{e}^-$  (1)

At cathode:  $\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$  (2)

Across Membrane: net positive charge from chromium solution to iron solution.

As the discharge continues, there is a gradual change in ratio of the charged to discharged species in the two solutions and a point is reached where like any other secondary battery, it must be recharged. A power supply is connected to the terminals and the reverse electrochemical reactions take place. Although Figure 3 shows only a single cell connected to the two Redox solutions, it is easy to see how a number of such cells could be connected together in parallel hydraulically and in series electrically. These stacks of cells closely resemble

fuel cell batteries and water electrolysis equipment.

The basic Redox system thus consists of a stack of cells, two pumps for circulating the Redox solutions, two tanks in which these fluids are stored, and some degree of control and switching equipment as with any other battery system. Several features of this system deserve further discussion.

1. The major feature of Redox systems that differentiate them from other battery systems is the complete independent sizing of the system storage capacity (kWh) by the selection of the tank volumes and solution concentration and the system power (kW) by the grouping of cells in the Redox cell stack. This is particularly significant for long term storage applications where the relatively inexpensive part of the system (chemicals and tanks) account for a high proportion of the system cost.

2. Since the charge and discharge reactions involve simple Redox reactions, there are neither any plating/deplating reactions, nor any solid compound phase changes. There are thus no fundamental cycle life limitations from an electrochemical standpoint. Also, no capacity losses or failures caused by shape change, slumping, shedding or other phenomenon that are related to electrode morphology changes can occur.

3. The mild operating conditions associated with aqueous solutions permits the use of inexpensive carbon, graphite and plastic materials for the tanks, piping, pumps and stack components.

4. The absence of any highly reactive or toxic ingredients will minimize the safety and environmental hazards.

5. The existence of an applicable industrial technology base in both the fuel cell and water electrolysis field is highly significant. These industries could well form the manufacturing base for the Redox hardware which is similar in many respects. This similarity has already been useful in making credible preliminary cost estimates for future Redox systems.

Although this paper is not intended to address the cost aspects of Redox systems in any detail, it should be emphasized that it is a flexible, low temperature aqueous system constructed using inexpensive materials and simple construction techniques. Preliminary cost studies indicate that Redox systems with only modest production rates are significantly less expensive than lead acid batteries for solar/wind applications with system features that lead to long life, high reliability and minimal operation and maintenance costs. With further development, Redox should be highly competitive for the utility storage application.



## System Features

In the final analysis, it is how well batteries of cells work together as a system that will determine the ultimate utility of various potentially attractive concepts. The most important advantages of Redox energy storage systems, particularly for applications where low maintenance levels are desired, become evident only after looking at the system as a whole. Battery systems that may be treated as a "black box" are the designer's desire. Batteries, however, are of course made up of a number of individual cells, hopefully matched, each having a pair of electrodes that always have varying levels of charge efficiency and performance decay modes. The battery system designer desires flexibility in the battery cycling scheme, exact cell to cell capacity matching, accurate state of charge measurement of the system as a whole, etc. Unfortunately, he cannot achieve these objectives with conventional battery systems and conservative design and frequent maintenance must be employed to assume proper system capability. In part, Redox systems can be treated as a large single cell when certain additional features are incorporated. These would allow the above listed system characteristics to be met in reality. This is all possible because a Redox system uses one set of solutions that is common to all the cells in the stack. The system features that have already been successfully incorporated into Redox equipment are as follows: state of charge readout, stack voltage control and system capacity maintenance. These represent very significant advantages of the Redox system and are discussed individually below.

### 1. State of Charge Readout

The state of charge of a system is simply the percent of the system capacity that is still in the charged state. The complement of this parameter is called the depth of discharge. The reversible open circuit voltage of a cell made up of two Redox solutions is a function of the logarithm of the ratio of the thermodynamic activities of the oxidized and reduced species. If the assumption is made that activities are equal to concentrations and the reactants are completely in balance  $(Cr^{+2}) = (Cr^{+3})$  when  $(Fe^{+3}) = (Fe^{+2})$  the voltage vs. depth of discharge relationship will follow that shown in Figure 4. It is simply a plot of the equation:

$$E = 1.075 - .059 \log \frac{Cr^{+3} \times Fe^{+2}}{Cr^{+2} \times Fe^{+3}} \quad (3)$$

One Redox cell in a stack, not connected to the load, can be used to monitor this open circuit voltage. A simple analog circuit can convert this voltage to either a depth of discharge or a state of charge readout. This reading will be for the

entire system since there is but one set of reactant fluids in use. The use of an open circuit voltage cell requires no charging, discharging or special maintenance of its own. The very distinctive voltage vs. depth of discharge relationship can be used to perform control or caution and warning functions that may be desired for any application.

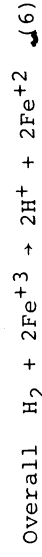
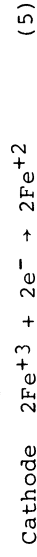
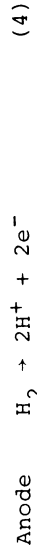
The shape of this voltage vs. depth of discharge curve is quite different from traditional battery electrodes in which the reactive species are solid in both states of charge and a relatively flat discharge curve is the rule. This means that for Redox systems a rather broad range of stack voltage from the beginning of discharge to the end of discharge is encountered. This can be corrected and even turned into an attractive feature with the use of trim cells.

### 2. Stack Voltage Control

The voltage of a Redox stack can be controlled to within any desired limits by the use of trim cells. These cells which are located at the end of a stack are switched in and out to maintain the voltage within required limits. Center tapping the stack to produce two different voltage levels for two sets of loads is also possible. Whether the voltage control feature or the multi-voltage level feature of this technique is used, it is important to remember that different parts of the system are not left at different states of charge. The system designer then has the option of using trim cell switching and/or power conditioning equipment to provide the required system voltage control.

### 3. System Capacity Maintenance

Probably the most important system feature of the NASA-Redox energy storage system is the rebalance cell. It is a cell that is an integral part of the stack. Its anode is a gaseous electrode that consumes hydrogen and its cathode is a regu-  
lar ferrous/ferric electrode. The electrode reactions are as follows:



The usefulness of the rebalance cell is appreciated only after the subject of reactant imbalance is fully understood.

Typically, the charging reactions in any type of battery system are less than 100% efficient. The side reactions that are usually associated with the desired reaction generally involve the formation of a gaseous product that may be vented to the atmosphere or recombined chemically within each individual cell. Cells using

lead, iron, cadmium or zinc negatives as well as Redox cells using the chromous/chromic Redox couple for the anode usually evolve a certain amount of hydrogen as the electrodes are being charged. The significance of this side reaction may be small, on a percentage basis, but its cumulative affects with repetitive charge-discharge cycling may be large depending on the degree of inefficiency associated with the cathode charge reactions. If it were assumed that the anode reaction was 95% efficient and the cathode reaction was 100% efficient, a gradual loss of cell capacity would ensue. A cell would lose 5% of its remaining capacity on each successive charge-discharge cycle. Most actual cells can have this capacity restored by going through an appropriate overcharge, deep discharge, or other prescribed capacity maintenance procedure. With Redox systems this process is handled on a continuous basis using the rebalance cell. When small amounts of hydrogen are produced at the chromium electrodes during the charge process, this results in the presence of the equivalent amount of ferric ion that is in excess of the amount of chromous ion that is produced.

Major Reaction at Chromium Electrode



Minor Reaction at Chromium Electrode

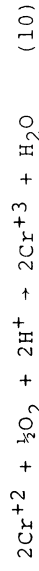


Exclusive Reaction at Iron Electrode



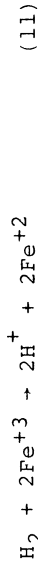
In a Redox system the hydrogen generated within all the cells is collected and directed to the hydrogen electrode of the rebalance cell. The cathode of the cell receives flow from the same iron solution that is used in the rest of the system. Figure 5 depicts a Redox system with one Redox cell, one open circuit voltage cell and one rebalance cell. The electrochemical reactions that occur (equations 4, 5, 6) are seen to be the exact opposite of the undesired side reactions that take place within the Redox cell. This cell is self-regulating since it only operates when there is hydrogen to consume. The open circuit voltage of a hydrogen/iron Redox cell is about 0.7 volts so energy is produced rather than consumed in the rebalance process in contrast to the situation in conventional batteries. Besides keeping all the cells of a Redox system in balance with respect to hydrogen evolution at the electrodes during the charging process, there are several other second order effects that can also be corrected for. These include any thermal chemical reduction of water by the chromous ion that might take place, any effects caused by the intrusion of air into the system, or gradual

escape of hydrogen before it is consumed in the rebalance cell. The air oxidation of chromous ion serves as an illustration.



The air oxidation results in the loss of hydrogen ion, the conversion of chromous ion to chromic ion, and an excess amount of ferric ion in the system relative to the remaining amount of chromous ion.

Hydrogen from an outside supply is fed to the rebalance cell where the reactions as listed above take place. Namely:



The hydrogen ion is restored and the ferric ion content is brought back into balance with the chromous ion content. This process of adding hydrogen from an outside source is referred to as external rebalance and the process of rebalancing the hydrogen generated within the system is called internal rebalancing.

Figure 6 shows the effect of adding the internal rebalance mode to a small laboratory (14.5 cm<sup>2</sup>) Redox flow cell. This reduction in the rate of capacity loss results from the recombination of most of the hydrogen evolved from the chromium electrode during charge. These small systems are not completely hydrogen tight so there is a residual capacity loss. Figure 7 shows the effect of adding the external mode to this same system. It is seen that the capacity can be completely restored. The Redox cell of the system (Figure 5) need not be withdrawn from service while the external rebalance process is carried out.

#### Complete Redox Systems

Larger sized cells and many more cells in the stack are needed for real applications. Figure 8 shows an exploded view of the individual cell parts showing the manifolds, inlet and outlet ports for the individual cells, gaskets, flow plates, etc. Figure 9 is a photo of a 200 watt twelve volt system that was constructed in January, 1979. It has twelve cells plus two trim cells in the stack as well as an open circuit voltage cell and a rebalance cell. The cells are one third of a square foot each in active area. The system delivers a peak power of just over 200 watts at a current density of 60 amps per square foot. The five gallon tanks give this system a capacity of about 400 watt hours. Currently, this is the largest full function Redox system that has been built. Plans call for the construction of a 2 kW (peak), 10 kWh full function system by the end of 1979. This size of system will permit verification of the major advantages and characteristics of complete Redox systems. These systems will be capable of all rebalancing requirements done on a continuous basis without removal of the stack from service. The

open circuit voltage cell will provide an accurate non-mechanical state of charge indication to drive any associated system logic. The trim cells will permit any reasonable voltage tolerance band to be maintained. Finally, the capacity loss will be limited to that caused by membrane crossover of iron and chromium ions. Membranes have already been developed that render this loss rate unimportant over periods of up to 20 years.

The current item which is pacing the overall technology is the membrane; specifically its resistivity and the stability of that resistivity with system operation. Currently, 30 amps/ft<sup>2</sup> can be obtained at 50% depth of discharge with a cell voltage of 0.9 V. For solar applications, the currently perceived requirement is about 50 amps/ft<sup>2</sup>. For electric utility applications where lower system costs are required, a performance of 100 amps/ft<sup>2</sup> under the above stated conditions is currently the goal. Considering the advances made over the preceding years, these improvements are viewed as fine-tuned technology improvements rather than enabling breakthroughs.

This work has been supported in part through the DOE-NASA Interagency Agreement E(49-28)-1002.

#### REFERENCES

1. Rosenblum, L., Bifano, W. J., Hein, G. F., and Ratajczak, A. F., "Photovoltaic Power Systems for Rural Areas of Developing Countries," NASA TM 79097, 1979.
2. Vinal, G. W., Storage Batteries, 4th ed., Wiley, New York, 1955, Chap. 6.
3. Thaller, L. H., "Electrically Rechargeable Redox Flow Cells," NASA TM X-71540, 1974.
4. "Redox Flow Cell Development and Demonstration Project, Calendar Year 1976," NASA TM-73873, 1977.
5. "Interim Cost Estimates for Advanced Battery Systems," Electric Power Research Institute, Palo Alto, Calif., EPRI EM-742, July 1978.
6. Alexander, S. S., and Hodgdon, R. B., "Anion Permselective Membrane," Ionics, Inc., Watertown, Mass., CONS/0108-1, July 1978 (NASA CR-135316).
7. Giner, Jose, et al., "Advanced Screening of Redox Couples," Giner, Inc., Waltham, Mass, NASA contract NAS 3-20794, Report in preparation.

# CONCEPTUAL DESIGN OF A 10-KILOWATT/500-KILOWATT-HOUR REDOX ENERGY STORAGE SYSTEM FOR SOLAR PHOTOVOLTAIC APPLICATIONS

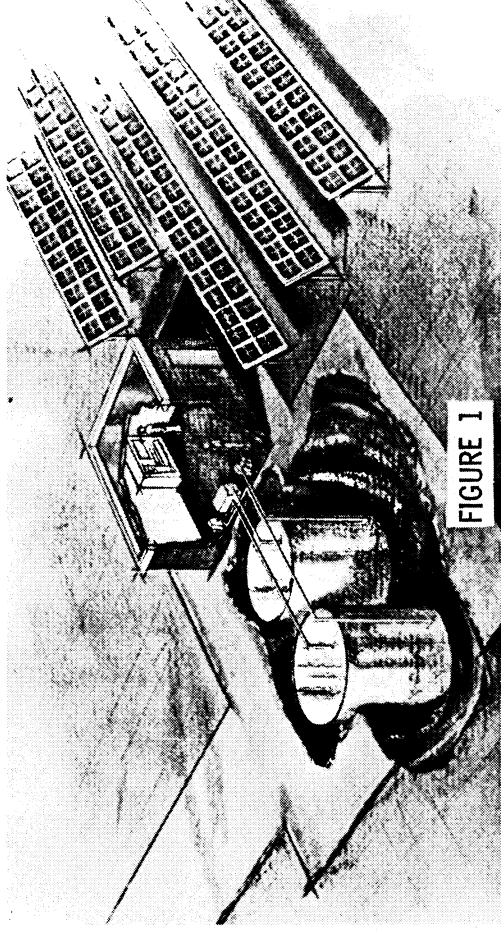


FIGURE 1

# CONCEPTUAL DESIGN OF A 10-MEGAWATT/100-MEGAWATT-HOUR REDOX ENERGY STORAGE SYSTEM FOR ELECTRIC UTILITY APPLICATIONS

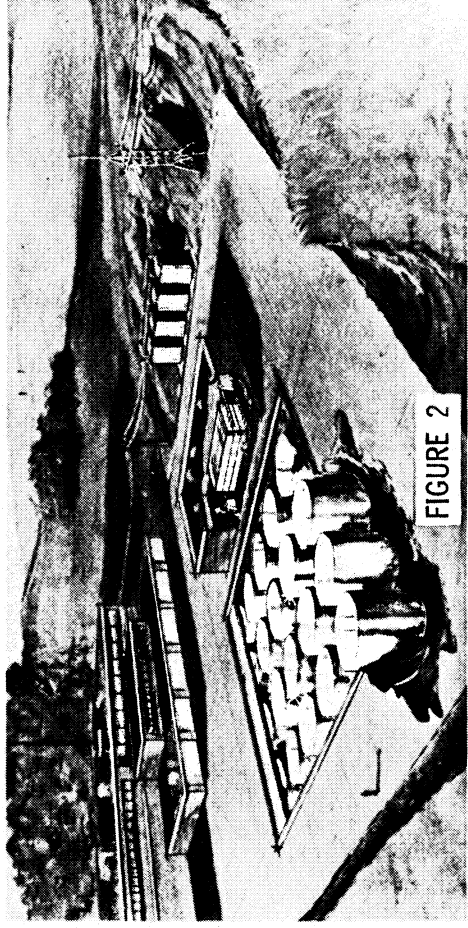


FIGURE 2

## TWO TANK ELECTRICALLY RECHARGEABLE REDOX FLOW CELL

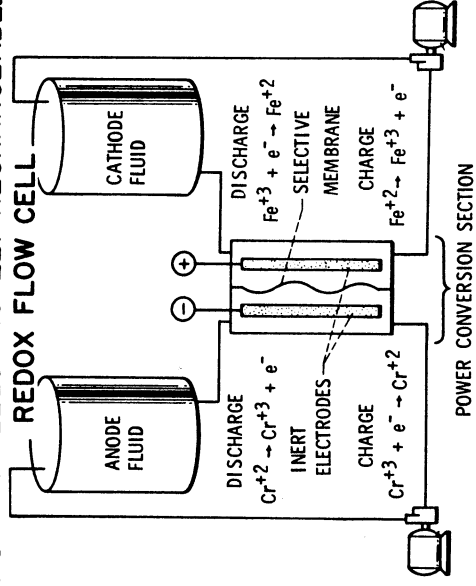


FIGURE 3

OPEN CIRCUIT VOLTAGE OF AN IRON - CHROMIUM REDOX CELL  
AS A FUNCTION OF DEPTH OF DISCHARGE

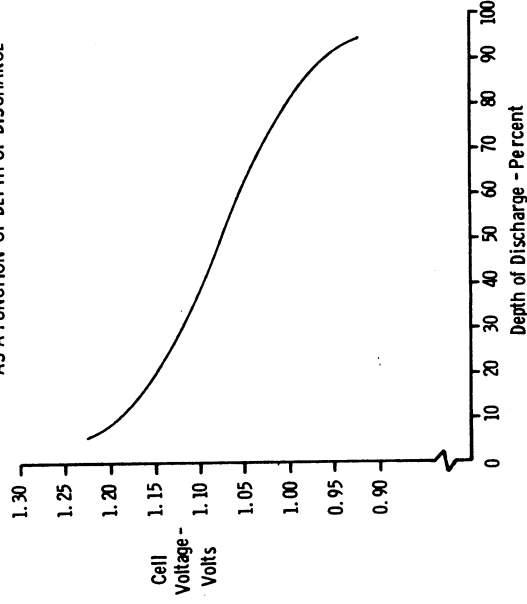


FIGURE 4

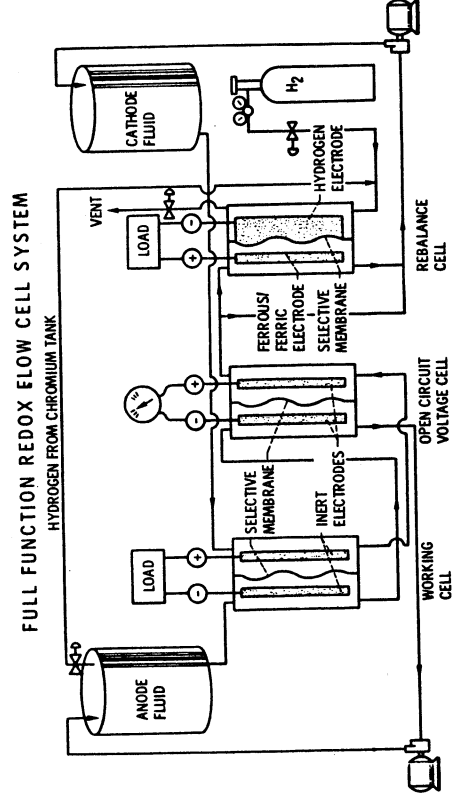


FIGURE 5

EFFECT OF REBALANCE CELL ON SYSTEM CAPACITY LOSS RATE

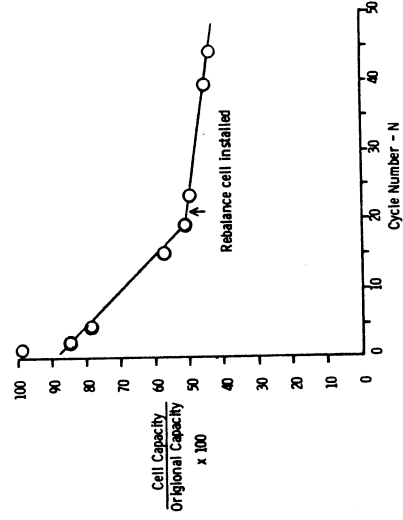


FIGURE 6

CAPACITY RETENTION OF A SYSTEM EQUIPPED WITH REBALANCE  
CELL USING BOTH INTERNAL AND EXTERNAL REBALANCE MODES

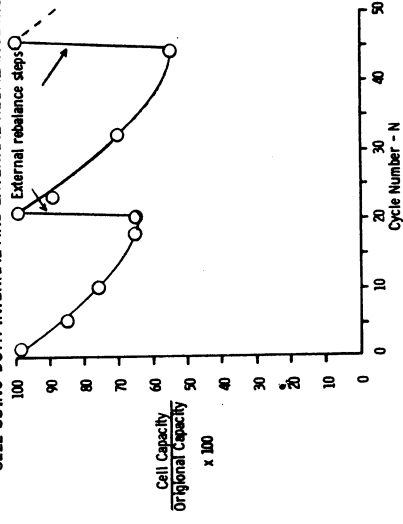
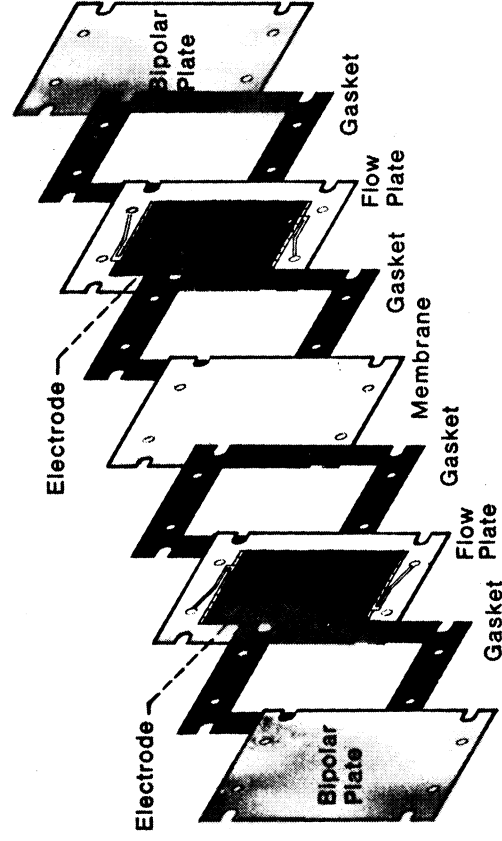


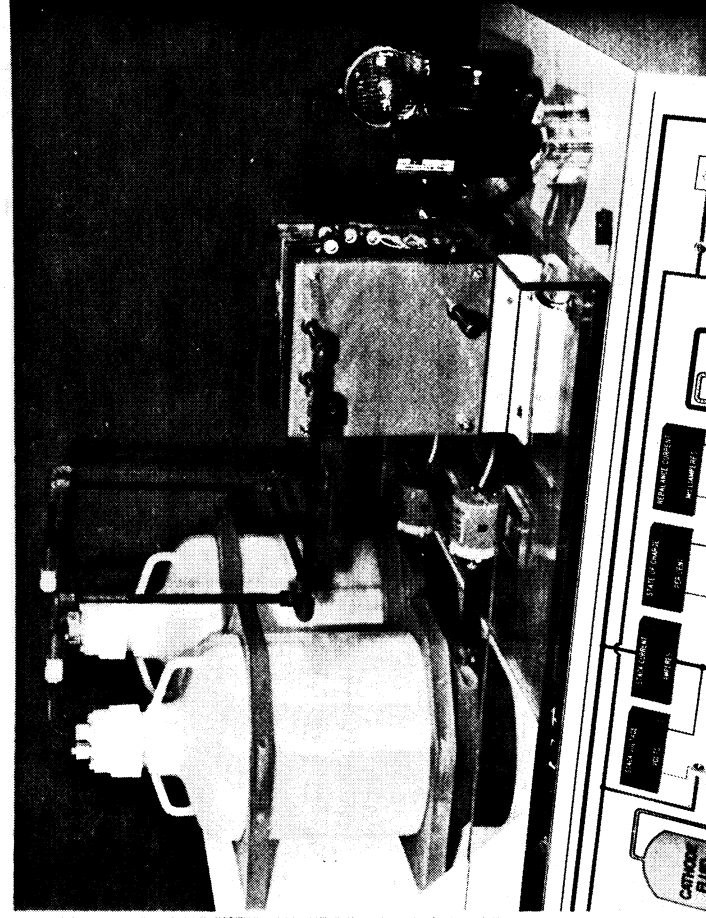
FIGURE 7

## REDOX SINGLE CELL COMPONENTS



**FIGURE 8**

## TWO HUNDRED WATT/FOUR HUNDRED WATT-HOUR FULL FUNCTION REDOX SYSTEM



**FIGURE 9**