

NASA TM-82854  
DOE/NASA/12726-16

DOE/NASA/12726-16  
NASA TM-82854

NASA-TM-82854

19820023583

82N 31459

# Design Flexibility of Redox Flow Systems

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

LIBRARY COPY

SEP 17 1982

LANGLEY RESEARCH CENTER  
LIBRARY, NASA  
HAMPTON, VIRGINIA

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

Prepared for  
Intersociety Energy Conversion Engineering Conference  
hosted by the Institute of Electrical and Electronics Engineers  
Los Angeles, California, August 8-13, 1982

#### NOTICE

This report was prepared to document work sponsored by the United States Government. Neither the United States nor its agent, the United States Department of Energy, nor any Federal employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

## **Design Flexibility of Redox Flow Systems**

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

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

Prepared for  
Intersociety Energy Conversion Engineering Conference  
hosted by the Institute of Electrical and Electronics Engineers  
Los Angeles, California, August 8-13, 1982

## DESIGN FLEXIBILITY OF REDOX FLOW SYSTEMS

Norman H. Hagedorn and Lawrence H. Thaller

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

### ABSTRACT

The characteristics inherent in Redox flow systems permit considerable latitude in designing systems for specific storage applications. The first of these characteristics is the absence of plating/deplating reactions with their attendant morphology changes at the electrodes. The second characteristic is the separation of power generating components (stacks) from the energy storage components (tanks). The final characteristic is the commonality of the reactant fluids which assures that all cells at all times are receiving reactants at the same state-of-charge. Consideration is given to a number of applications, each of which takes advantage of one or more of the inherent characteristics of Redox flow systems. These various applications span a spectrum of power and energy requirements from small, uninterruptible power supplies, through stand-alone photovoltaic and wind sites to electric utility central stations. Finally, an update on the status of the NASA Lewis Redox system technology will be provided, focusing upon electrode and membrane developments and system cost projections.

### INTRODUCTION

The NASA Redox concept has been under development since 1974. It is but one of several flow battery concepts that have received some support from the Department of Energy (DOE) as potential contributions to energy conservation and renewable energy sources. The Redox system is unique in that it is based on the use of two fully soluble redox couples as reactants. Discussion of the Redox concept can be broken down into two general areas. The first gives consideration to a series of unique system features that have been conceived and demonstrated at the laboratory level by researchers at NASA-Lewis Research Center (LeRC). The second area of discussion considers the associated key technologies that have been brought to various stages of maturity by the researchers at LeRC and their contractors. As advancements take place in these key technologies, the storage applications that are built around the unique system features of Redox, and proposed in this paper, will become more practical and realizable.

Earlier reports have addressed some of the unique system features of Redox systems (refs. 1

and 2) which will therefore be covered only briefly here. The status of the three primary technology areas (membrane properties, electrode performance and flow requirements) have also been reported elsewhere (refs. 2 to 4). It is the primary intent of this paper to briefly review the unique system features associated with pure redox systems and then deal at length with how these features can be incorporated in various storage system concepts for specific applications. Whether or not these systems concepts represent practical ideas will depend in part on the relative states of maturity of the three aforementioned technology areas and in part upon the ill-defined costing and market factors that come into play with any new technology. A brief technology status summary will be presented at the conclusion of the paper along with the most recent information regarding the encouraging costing aspects of the system.

### SYSTEM FEATURES AND CHARACTERISTICS

Redox systems in their simplest form are based on the use of two fully soluble redox couples that are electrochemically oxidized and reduced at inert electrodes. Solutions of these two redox couples are separated by a membrane that must be very selective so as to almost completely preclude the transfer of redox reactant ions from one solution to the other. At the same time the membrane must allow free passage of the ions used to maintain charge neutrality within the solutions. Considering the Redox system currently under investigation at LeRC, acidified solutions of the chromous/chromic and ferrous/ferric redox couples serve as the anode and cathode reactants during discharge, while a highly selective membrane which permits passage of chloride and hydrogen ions (to the virtual exclusion of iron and chromium ion) is placed between the two solutions. Porous carbon felts (catalyzed, in the case of the chromium electrode, ref. 3) serve as the inert electrode structures. The preponderance of the redox fluids are stored in tanks outside of the cell described above and are pumped through the cell as per Fig. 1. The reactions that take place within the porous electrodes start and end in the liquid state. Considering the discharge reaction in the acidified iron solution for example, the entering solution contains a mixture of iron in the plus two and plus three valence states along with the associated chloride ions and hydrogen ions. As the cell is discharged some of the iron ions undergo electro-

chemical reduction as they flow through the porous electrode and pick up electrons ( $\text{Fe}^{+3} + e^- \rightarrow \text{Fe}^{+2}$ ). The important feature of a classic redox couple is that the reactants in both states of charge are fully soluble. This factor is significant when batteries, i.e., multi-cell groupings, are considered. Figure 2 shows how individual cells are connected together in a bipolar manner to yield a stack of cells with a voltage that is the sum of all the individual cell voltages. The redox solutions are fed to the stack via a primary manifold which in turn feeds each one of the cells. The use of a common fluid in all of the cells results in the fact that all the cells will always be at the same state of charge relative to one another. This does not say that the two redox solutions necessarily will always be in balance; but, with the Redox system, techniques have been developed that can maintain the two solutions in electrochemical balance. The reader is referred to reference 2 for a fuller explanation of this system-related feature. As noted above, the use of solutions that are common to all the cells results in all the cells being at the same state of charge. If, in addition, the solutions are in electrochemical balance, then the output voltage of a cell which is maintained at open circuit can be used to indicate the state of charge of the system as a whole. This is based on standard half-cell potentials and the associated Nernstian corrections for the existing state of charge (ref. 2). Figure 3 schematically illustrates what is called a full-function Redox system.

The commonality-of-fluid aspect of cells in a redox system results in a further unique feature available to these systems. This is illustrated with the help of figure 4. This figure depicts a full-function Redox stack with a rebalance cell and an open circuit voltage cell located at the left hand end of the stack. A single hydraulic path for each of the two fluids is employed. The majority of the cells within the stack are working cells. At selected points along the stack provision is made for current taps. Although very thin bipolar plates can be used to connect one cell to the next, a thicker plate that can serve to conduct the current out of the stack in a lateral manner must be employed at either end of the stack as well as at intermediate points along the stack where intermediate voltage levels can be selected. Assuming 0.9 volt per cell, then from point A' to B' a potential of 12.6 volts would exist. From point A' to C' a selection of three voltage levels is permitted; 50.4 ± 1.8 volts. This use of "trim" cells thus permits a form of voltage regulation to be exercised on the stack.

Conversely, by applying the proper voltage across AB or AC the redox fluids can be charged. It should be noted that the solutions simultaneously can be charged by some cells and discharged by others by appropriately selecting the charging voltage and the load resistance. In fact the charging process using the AB terminals and the discharging process using the A' B' or A' C' 2 or 3 terminals result in the equivalent of a DC-to-DC transformer. This feature is used in several of the following specific examples.

The basic reasons for the flexibility of Redox systems in comparison to other electrochemical systems, both flow and nonflow, can be summarized as follows: (1) the use of electroactive materials that are soluble in both states of charge permits a separation of the storage capacity of the system (size of storage tanks) from the power-producing capability of the system (size and number of cell stacks); (2) the commonality of fluids between cells assures that all the cells are at the same state of charge. The trim cell, the open circuit voltage cell and the DC-to-DC transformer features are made possible by this feature; (3) the use of soluble redox couples of course precludes the usual plating/deplating of solid/solid type electrochemical reactions and their associated life-limiting feature.

There are several undesirable characteristics that are associated with the general class of batteries in which a common electrolyte flows through a group of cells that are connected electrically in series and hydraulically in parallel. The shunt current problem is probably the best known of these undesirable characteristics. The second and often disregarded characteristic is that pumping energy is expended in the movement of liquids from the storage tanks to the cell stack and back. As might be expected, there exists a minimum in the sum of the shunt losses and pumping losses that is somewhat dependent on the flow rate of the circulating fluids. This three-way trade off and optimization is fully covered in reference 4. In brief, it can be stated that the sum of the losses reduces the round-trip efficiency of a flow battery system from 5 to 10 percentage points below that expected from single cell performance. That is, if a single cell yields a DC-to-DC round-trip watt-hour efficiency of 80 percent, then 70 to 75 percent would be the expected efficiency from a stack of practical size when pumping and shunt losses are considered. The following examples of specific applications were not all analyzed to the required depth to be able to determine round-trip efficiencies.

A further consideration that is not addressed in detail in each case was the rate of capacity loss due to the cross diffusion of reactant species from one solution into the other. In certain cases it was assumed that premixed reactants would be used. Premixed, as the nomenclature implies, assumes that both of the starting solutions contain equal concentrations of iron and chromium chloride. In these cases there would be no loss of capacity with time due to cross-diffusion. From an electrochemical standpoint, the iron ions in the chromium solution would act only as a diluant since they would be present in the reduced state and would not undergo further reduction or oxidation unless potentials outside of those normally expected would occur.

The volume of reactants required by Redox systems is of prime importance in certain cases and of little concern in others. The volumes actually needed for a particular application can be estimated using a combination of chemical rules and selected assumptions. If a solution contained active material at a concentration level of 1.0 Molar, then one liter of it contains enough ions to produce 26.8 Ahr (1.0 F) of electricity. If 2.0 M

solutions were used, this required volume would be halved. Flow considerations and the associated pumping requirements suggest that excess reactants should be used so that the cycling would be from, for example, 10 percent to 90 percent depth of discharge. Thus, approximately 25 percent excess reactants would be added to the actual stoichiometric requirements. If allowance were to be made for, say, 25 percent crossmixing during system life, a further 33 percent increase of this quantity, to 1.67 times the stoichiometric requirement, would be called for. For premixed reactants, where cross-mixing is not a factor, this last increment is not required. Thus, the volume requirement for mixed reactants would be about 25 percent less than for initially unmixed reactants. (Table 1 assumes an average operating voltage of 0.9 V in calculating the estimated solution volumes.) In like manner, preliminary estimates of stack sizes can be made. Current cells at room temperature can operate over the range of 31 to 111 milliamps per  $\text{cm}^2$  depending on the tightness of the membrane used. Very loose membranes of the type used with premixed solutions would correspond to the 111  $\text{ma}/\text{cm}^2$  operation. Roughly 1.1 to 3.3 $\text{M}^2$  (11 to 37  $\text{ft}^2$ ) of active area is thus required per kW of normal output. Typically the peak power output is about twice that of the normal output. The thickness of a cell depends on the materials used - particularly for the bipolar plates. The baseline cells are between 4 and 5 mm. The resultant stack volume estimates would range from 4.4 to 16.5 liters/kW. To this volume must be added that associated with the framing around the active area, the end plates and tiebolts, and the piping associated with the stack. When viewed in the context of table 1, the volume of the stack portion of the system is much smaller than the storage portion of the overall system.

## SPECIFIC APPLICATIONS

### 1. Reserve Power Applications

Reserve power applications are those applications where energy is stored for some indefinite time for use in the future. Typically these systems are maintained on trickle charge until some point in time when the grid power is interrupted and the storage system is called upon to deliver energy for several hours. This general application area can be further divided into uninterruptable power supply applications where no interruption of service is permitted and standby applications where delays of several seconds can be tolerated without creating a problem. A third class of application referred to as grid-buffered is also included in this section. Here the objective is to create a bus totally isolated electronically from the grid yet supplied via an energy vector from the grid when it is operational and which can provide uninterrupted power if the grid becomes unavailable.

#### a) Uninterruptable Power Supply (UPS)

One possible UPS schematic is shown in figure 5. The system floats on the bus through an AC/DC converter. The main stack is shown with a variety of intermediate voltage taps as might be

required by a system used by an electric utility at a substation site. The system requirements only call for a short storage duration of say four to eight hours at a power level of several kW. Small pumps would continuously circulate the solutions and a trickle charge would make up for the shunt losses in the stack. As soon as the system is called into service the main pumps are turned on to increase the rate of flow of the fully charged solutions through the stack. These pumps are sized to provide the required flow rates at the deepest expected depth of discharge (see ref. 4). In as much as a rather low ratio of solution volume to membrane area is associated with this system, the rate of capacity loss over the course of time due to cross-mixing would be expected to be rather rapid. For that reason it is suggested that premixed solutions be used. If the application should call for an AC output, a combination inverter-converter would be required.

#### b) Backup Power

Figure 6 shows one suggested schematic for the case where the "instant-on" feature of an UPS is not required. In this case there is no fluid flow through the main stack, thus there is no shunt current loss associated with this portion of the system. The small trickle charging stack (and its small pumps) keeps the fluids fully charged, and provides the power for the main pumps to pump the fresh solutions into the main stack when full power is called for. An alternative would be to use a small lead acid battery to power the main pumps until the Redox stack had received fresh solutions, at which time the pumps would switch to Redox power and the battery would be restored to full charge, also by the Redox stack. As in the preceding case, the stack output can be multilevel DC or AC depending on the particular requirements.

#### c) Buffered Grid

The case referred to as buffered grid is a simple modification of the backup power case where the output of the main stack is used to feed a DC to AC inverter in a continuous manner. The Redox fluids act as an energy transfer fluid from the main grid to a secondary bus that is decoupled in the electronic sense from the primary grid. This modification now requires a charging stack and pumps that are closer in size to the discharging stack and pumps. Situations where electromagnetic interference with special equipment located on the secondary bus cannot be tolerated would suggest this type application.

### 2. Stand-Alone Applications

Stand-alone is the term usually applied to applications that are not connected to any grid network. Remote installations where solar photovoltaic or wind energy is the primary source of energy are in this classification. Usually storage is required for times when the sun doesn't shine or the wind doesn't blow. In this type application a certain degree of voltage regulation is required. The storage duration and voltage level can vary depending on the particular installation, but is

considerably larger (~ 50 hr) than for other applications encountered. For low power requirements and short distribution runs of wire, the use of DC power in the vicinity of 110 volts has been found to be adequate (ref. 5). Reference 6 specifically addresses this application and the results are only summarized here.

There are four suggested ways of connecting the intermittent source to a Redox system for a stand-alone application. They all make use of trim cells to provide the required voltage regulation. The basic system is a full-function system as depicted in figure 3 with appropriate switching levels as illustrated in figure 4. Figure 7 depicts the four configurations that might be used here. For simplicity, the pumps and tanks are not shown. In case A the Redox stack floats on the bus, and the switching action of the trim cells is used to maintain the proper charging and discharging voltage. In case B, all the power from the solar array or the wind turbine is fed across a fixed segment of the Redox stack and the required voltage regulation is provided by the switching action on the load side of the stack. In case C a greater degree of flexibility is added by using switching on the supply side as well as the load side of the stack. This feature permits the Redox solutions to be charged at optimum rates compared to the previous case. Finally in case D the Redox solutions are charged using a separate stack of cells than are used for the discharge process.

A preprototype 1.0 kW (2.0 kW peak) Redox system with an output of 120 V DC has been constructed and operated as configured in case A and B to provide some early insights as to the operational compatibility of a Redox system with a solar photovoltaic array. The combined system operated in a fully satisfactory manner. Details of that testing are given elsewhere (ref. 7).

### 3. Electric Utility Applications

There are a number of potential applications where the storage of electrical energy is seen as a financially beneficial alternative to other processes for meeting electrical demands. The main application that is considered here is the case of a large electric utility using excess baseload capacity to charge up large energy storage devices during off-peak hours for use during times of high demand. Storage is but one of several options available, and electrochemical storage but one of several competing concepts. The utility may be a generating utility that is primarily interesting in peak shaving (2 to 5 hr) or the utility may be a distributor of purchased power that is more interested in longer duration load leveling applications (5 to 10 hr of storage). Storage is also of interest to large industrial users of electricity who are interested in taking advantage of the benefits of time-of-day pricing of electricity and/or reducing their peak demands on the grid. These cases differ from the earlier cases of reserve power applications in that their function was to store energy for some undetermined time in the future, whereas in a utility environment demand is more or less scheduled on a regular basis (usually daily). With a much more formalized

charge and discharge schedule, several efficiency saving features can be added to the basic Redox concepts presented above. Also these applications tend to be multi-megawatt in size, which suggests much different handling of heat loads than in some of the earlier examples.

The initial patent covering Redox flow cells (US Patent 3,996,064) depicts what is called the four-tank version of Redox along with the more often referred to two-tank version. The difference lies in whether the exiting Redox solutions are remixed with the remaining solution or are stored in separate tanks. There is a definite voltage advantage in the case of the four-tank arrangement, compared to the two-tank case, where the available energy contained in the fresh solutions is partially degraded by having the discharged solutions mixed with the fresh. This four-tank approach assumes a certain degree of flow rate control is available and that trim stacks can be used. As pointed out in reference 8 a constant discharge voltage results from this type of system arrangement and flow scheduling. Figure 8 shows this type of arrangement where a flexible liner within the two storage tanks produces the equivalent of a four-tank system.

### Summary of Applications

The list of applications covered here is not intended to be exhaustive but only to cover the diversity of possible applications that the group at NASA LeRC has examined over the course of the evolution of Redox technology. Although it is not the intent of this paper to address the volume and energy density aspects of these systems beyond the rough estimate given in the earlier sections, it is evident that these systems are not applicable to mobile applications. Some of the applications that have been suggested and/or explored by others have not been mentioned here because they do not represent a new system configuration, just different volume-to-area ratios of solution and membrane; or they have never been thought through in terms of hardware. Investigators have looked at Redox solutions as energy transfer media in ocean thermal energy conversion (OTEC) applications. They have also considered Redox for underwater applications where the solutions could serve as pumpable ballast fluid. In addition, they have looked at Redox in regenerative braking applications where the high cycle life of redox couples could be of benefit. The unique features of this technology permits system variations that are limited only by the imagination of the design engineer.

### STATUS OF REDOX SYSTEM AND COMPONENT TECHNOLOGY

As mentioned above, the ability of a particular Redox system design to satisfy any of the applications discussed in this paper will depend on membrane and electrode properties, the reactant flow characteristics and system and reactant costs. Superimposed upon all these elements, in a very significant way, as determined during the past year, is the effect of raising the temperature of operation.

From a system standpoint, of course, operation of a reasonably-sized electrochemical storage system must occur at elevated temperature, in order to reject waste heat to the environment. This is one of the great secrets, often "swept under the rug" during discussions of electrochemical storage system design and cost. This consideration, however, was not our impetus for investigating elevated temperature operation.

It had been determined (ref. 7) that the uncharged chromic ion exists in the form of two complexes: the penta aquo mono chloro chromic, which is electrochemically active; and the hexa aquo chromic, which is not. At room temperature the equilibrium concentrations of these species are about equal and the rate toward equilibrium is quite slow. As a result, when charging a cell with reactants equilibrated at room temperature, depletion of the active "penta" specie results in a rapid rise in the voltage required for constant-current charging (fig. 9), or a precipitous drop in charge acceptance rate for constant voltage charging (fig. 10). However, if the chromic chloride solution is heated to temperatures above 40° C, the rate of equilibration becomes rapid and strongly favors the active "penta" specie. Even if such a treated solution is quenched back to room temperature, the "penta" concentration remains high. For comparative purposes, figures 9 and 10 include charging curves for cells with heated then quenched, chromic solutions. The striking improvement in charge acceptance results in a much greater utilization of the reactants and a much improved cycle energy efficiency.

Another advantage of operation at elevated temperature is the reduction in the electrolyte and membrane resistivity. The effect of increasing temperature on cell resistivity for three states-of-charge is shown in figure 11. The indicated resistivity reduction of about 40 percent in going from 80° F (27° C) to 150° F (66° C) will also greatly improve cycle energy efficiency. This can be seen in figure 12, which presents charge and discharge polarization curves at 50 percent SOC for 27° C and 66° C, respectively.

The ability to operate Redox cells with totally mixed reactant solutions, as suggested in the discussion of uninterruptable power supplies, would offer many advantages to the Redox system. By definition, cross-mixing of reactants would no longer be a factor. Microporous separators could be used, offering significantly lower cell resistance and cell cost. Also, any tendency toward solvent transfer could be countered easily by applying pressure or simply by pumping fluid back to the diminished reservoir. Figure 13 compares the constant-current charging curves (with mixed reactants) for a conventional cell and a cell having a microporous separator. Figure 14 compares charge and discharge polarization curves for these same two cells, except the standard cell contained unmixed reactants. In the absence of any attempt to optimize this system, the associated penalties seem to be a lower coulombic efficiency and a somewhat greater hydrogen evolution rate on charge.

The four-tank system discussed previously, and depicted in figure 8 also has been briefly evaluated experimentally. Because flow rates were desired to be only 1.5 times the stoichiometric

flow requirement, it was necessary to measure and control flows as low as 7 cm<sup>3</sup>/min, to a 300 cm<sup>2</sup> single cell. Difficulties in the control of flows resulted in some anomalies as seen in figure 15, where cell performance actually improved during the second discharge stage, probably due to rising flow rates. Superimposed on the figure is the expected performance of a conventional "two-tank" system operating under the same conditions. The performance advantage accruing to the four tank system would result in as much as a five percentage point improvement in energy efficiency.

#### SYSTEM COST PROJECTIONS

As mentioned earlier, projected system costs are always a significant factor in determining the viability of a storage system for a particular application. Thus, Redox reactant costs are an important issue, especially in the case of a system using mixed solutions, where the necessary quantities of reactants for a given capacity are greater by about 50 percent. Several methods for producing Redox reactants from chromite ore, which contains both iron and chromium, have been developed and evaluated in terms of the projected price for mass-produced reactants. The results of these studies, which were carried out by the Allied Chemical Corp. and the Charles River Associates (refs. 9 and 10) are summarized in table 2. Also in the table is an entry for United Technologies Corp., which value was assumed by that company in a cost study of mass-producing complete Redox systems (ref. 11). In table 3 is presented the Redox system factory cost as originally developed by UTC, and what that cost becomes when adjusted to reflect the estimated cost of reactants produced by chlorination of pre-reduced chromite ore, \$11.31/kWh. Needless to say, the results of these cost studies are very encouraging and suggest that Redox systems, in addition to having great design flexibility for a wide range of applications, can be economically competitive as well.

#### TECHNOLOGY DEVELOPMENTS

Recently, the major focus of the electrode technology development effort at NASA-LeRC has been to define production standards for carbon felt for chromium electrodes. The goal for such standards is to enable the reproducible preparation of catalyzed chromium electrodes which will have a high hydrogen overpotential yet be active for the reduction and oxidation of chromium ions.

Typically, the rayon felt precursor is preheated to 370° C to 427° C in a nitrogen atmosphere, then partially or totally graphitized at temperatures greater than 1200° C. Catalyzed electrodes have been prepared from felts treated at 1250° C, 1350° C, 1500° C, 1650° C, 1800° C and 2300° C. For each temperature, both scoured and unscoured felts have been evaluated. "Scouring" is the cleaning with a solvent to remove any sizing or other contamination.

Figures 16(a) and (b) show the cumulative amount of hydrogen generated during the charging of each of the cells containing the various test electrodes. Both figures indicate a dramatic decrease in hydrogen evolution for electrodes



prepared from felts processed at greater than 1650° C. Reference 12 covers this topic in more detail.

The membrane technology development effort has primarily been directed toward improvement of the resistivity and selectivity of the standard CD1L formulation consisting of a copolymer of vinylbenzyl chloride (VBC) and dimethylamino ethylmethacrylate (DMAEMA) on a calendered modacrylic substrate. This standard formulation results in a  $\text{Fe}^{+3}$  diffusion rate of  $20 \mu\text{gFe}^{+3}/\text{hr-cm}^2 - \text{M/A}$ , and a resistivity in 0.1 N HCl of  $4.2 \text{ ohm-cm}^2$ . In a working cell, resistivity averages about  $3.5 \text{ ohm-cm}^2$  at room temperature and  $2.0 \text{ ohm-cm}^2$  at 65° C. One approach has been to use thinner, woven and nonwoven substrates of various materials. Due to such characteristics as cracking, nonadhesion, etc., associated with these substrates, the standard membrane in use at the beginning of the year remains the best. References 12 and 13 treat this subject in much greater depth.

#### CONCLUDING REMARKS

Because of unique characteristics inherent to Redox systems, among these being the absence of electrode morphology changes, the impossibility of various groupings of cells in a system being at different states of charge and the ability to independently size the energy and power-producing portions of the system for specific applications, such systems potentially offer a great deal of design flexibility and a wide range of capabilities. Possible Redox storage applications range from low-power uninterruptable power supplies to utility load leveling, from remote village sites with intermittent sources to a fluid isolation link between an electric source and an ultimate load, to a DC to DC converter. Recent contractor studies also indicate that Redox systems can be economically viable in the various applications.

Some of these varied applications would call for changes in the focus of the present technology effort, such as considering in greater depth the use of mixed solutions and microporous separators. Because of the potential benefits and attractive cost projections, the Redox concept is a fruitful area for continued research and development.

#### References

1. L. H. Thaller, "Electrically Rechargeable Redox Flow Cells," NASA TMX-71540, 1974.
2. L. H. Thaller, "Redox Flow Cell Energy Storage Systems," DOE/NASA/1002-79/3, NASA TM-79143, 1979.
3. R. F. Gahn, J. Charleston, J. S. Ling, and M. A. Reid, "Performance of Advanced Chromium Electrodes for the NASA Redox Energy Storage System," DOE/NASA/12726-15, NASA TM-82724, Nov. 1981.
4. N. H. Hagedorn, M. A. Hoberecht, and L. H. Thaller, "NASA Redox Cell Stack Shunt Current, Pumping Power and Cell Performance Trade-Offs," DOE/NASA/12726-11, NASA TM-82686, 1982.
5. L. Rosenblum, W. J. Bifano, G. F. Hein, and A. F. Ratajczak, "Photovoltaic Power Systems for Rural Areas of Developing Countries," NASA TM-79097, 1979.
6. N. H. Hagedorn and L. H. Thaller, "Redox Storage Systems for Solar Applications," DOE/NASA/1002-80/5, NASA TM-81464, 1980.
7. N. H. Hagedorn, "NASA Preprototype Redox Storage System for a Photovoltaic Stand-Alone Application," DOE/NASA/12726-8, NASA TM-82607, 1981.
8. A. W. Nice and N. H. Hagedorn, "A Redox System Design for Solar Storage Applications," DOE/NASA/12726-14, NASA TM-82720, 1981.
9. Allied Chemical - Final report, Contract DEN 3-250, in preparation. "Study to Establish Cost Projection for the Production of Redox Chemicals," DOE/NASA/12726 -
10. Charles River Assoc. - Final report, Contract DEN 3-251, in preparation. "Study to Establish Cost Projection for the Production of Redox Chemicals," DOE/NASA/12726 -
11. K. Michaels and G. Hall, "Cost Projections for Redox Energy Storage Systems," DOE/NASA/0126-1, NASA CR-165260, United Technologies Corp., South Windsor, CT., Feb. 1980.
12. 1981 Annual Report - Redox Project - in preparation.
13. Ionics, Inc. - Final report, Contract DEN 3-204, in preparation. CR-167872, "Permselective Anion Membranes," DOE/NASA/12726 -

TABLE 1. - IDEAL SOLUTION VOLUMES FOR REDOX APPLICATIONS  
[Assumed operating voltage, 0.9 V]

| Situation                    | Total Solution Volume (2 solutions) per kWh |        |
|------------------------------|---|--------|
|                              | Ft <sup>3</sup>                             | liters |
| 1.0M Stoichiometric          | 2.93  | 82.91  |
| 2.0M Stoichiometric          | 1.46  | 41.46  |
| Premixed, 1.0M each, Stoich. | 2.93  | 82.91  |
| 1.0M, Stoich. + 25 %         | 3.66  | 103.64 |
| 1.0M, Stoich. + 67 %         | 4.89  | 138.57 |

TABLE 2. - SPECIFIC TOTAL REACTANT COST (1M FeCl<sub>2</sub>, 1M CrCl<sub>3</sub>, 1N HCl)  
BASED ON A PRODUCTION RATE OF 25,000 ton/year (22,727 METRIC ton/year)  
ON A CHROMIUM BASIS, AND A 30 PERCENT RETURN ON INVESTMENT

| Production Method  | Cost (\$/kWh) |
|--|---------------|
| Allied Chemical Corp.*   |               |
| -- Reductive Chlorination of Chromite Ore  | 21.73         |
| -- Electrolytic Reduction of Sodium Chromate   | 17.02         |
| -- Methanol Reduction of Sodium Chromate   | 14.00         |
| -- Chlorination of Prereduced Ore  | 11.31         |
| Charles River Associates*  |               |
| -- Production from Ferrochrome   | 8.77          |
| United Technologies Corp. (baseline)   |               |
| -- FeCl <sub>3</sub> @ 19¢/lb (42¢/Kg), CrCl <sub>3</sub> · 6H <sub>2</sub> O @ 32¢/lb (70¢/Kg)<br>and HCl @ 29¢/lb (64¢/Kg) | 22.26         |

\*30 percent ROI

TABLE 3. - SPECIFIC TOTAL SYSTEM FACTORY COST BASED ON PRODUCTION OF  
100,10 MW/100 MWH SYSTEMS PER YEAR: (a) AS DEVELOPED BY UNITED  
TECHNOLOGIES CORP.; (b) AS MODIFIED TO REFLECT LOWER REACTANT  
AND TANKAGE COSTS (ALLIED CHEMICAL CORP.)

|   | System<br>Factory Cost |
|---|------------------------|
| a. 2M reactants @ \$22.26/kWh, tankage<br>@ \$.60/gal. (\$.158/l)   | \$62.27/kWh            |
| b. 1.5M reactants @ \$11.31/kWh, tankage<br>@ \$.24/gal. (\$.063/l) | \$44.80/kWh            |

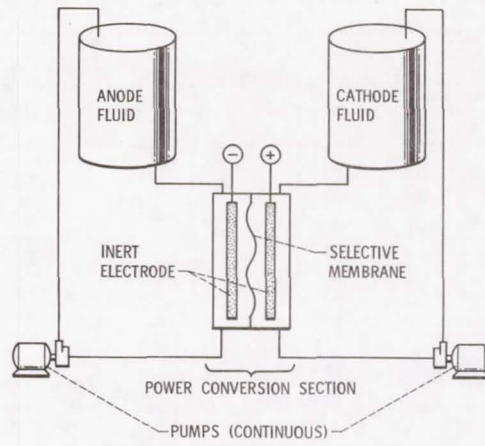


Figure 1. - The Redox flow system concept.

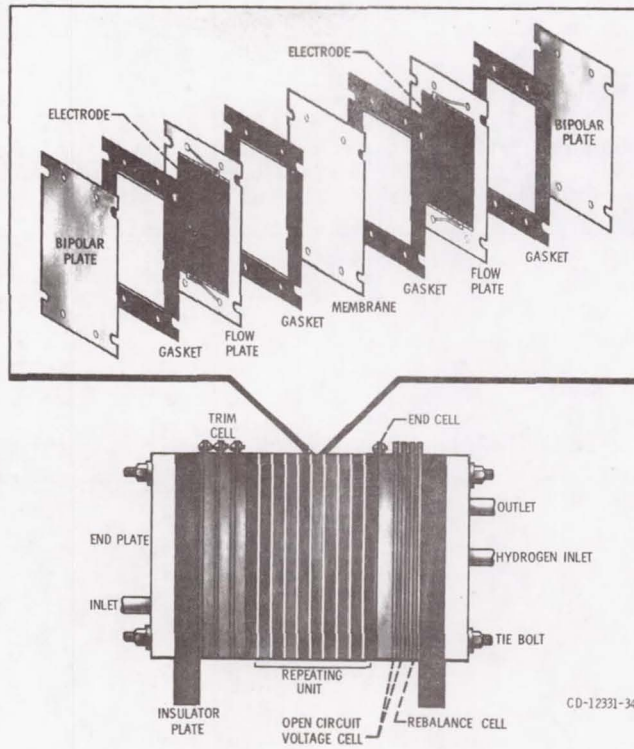


Figure 2. - The bipolar Redox stack, and an exploded view of a typical interior cell.

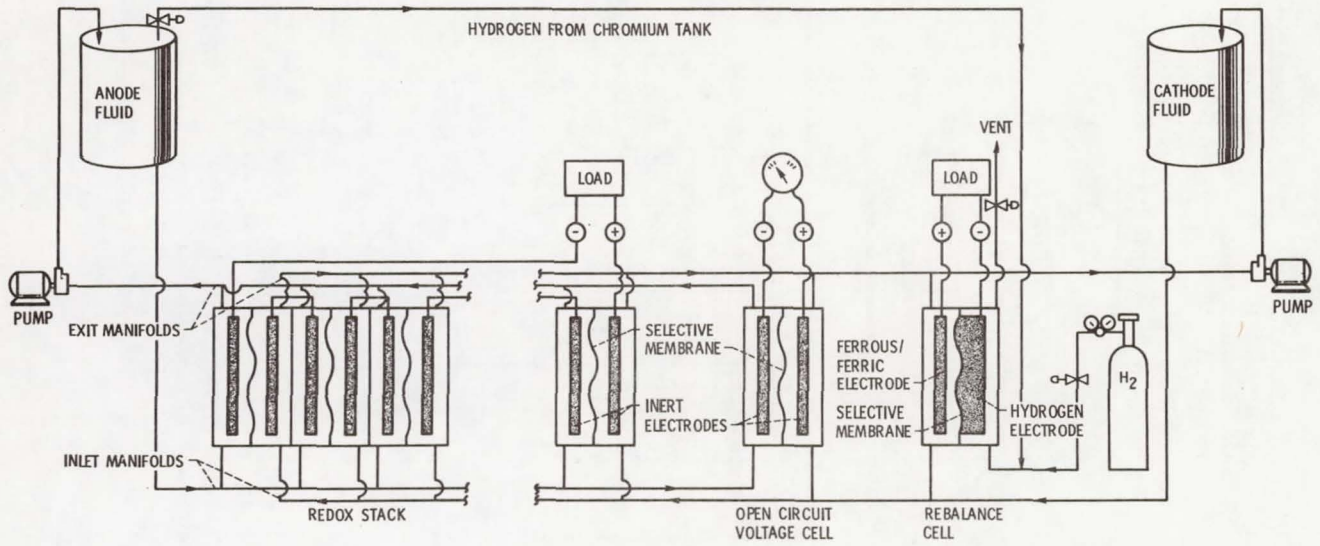


Figure 3. - The full-function Redox flow system including standard cells, open-circuit (charge indicator) cells and hydrogen rebalance cell.

ILLUSTRATED STACK HAS THE FOLLOWING FEATURES:

1. NOMINAL OUTPUT AT .9 VOLTS/CELL - 12.6 V AND  $50.4 \pm 1.8 V$
2. SINGLE HYDRAULIC PATH
3. REBALANCE CELL AND OPEN CIRCUIT VOLTAGE CELL INCORPORATED INTO STACK

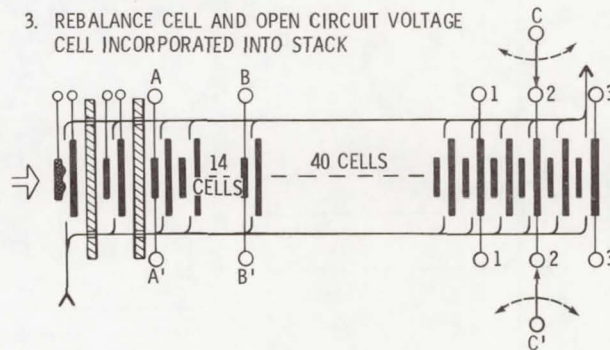


Figure 4. - Full-function Redox stack with multiple voltage capability and trim control of charge and discharge.

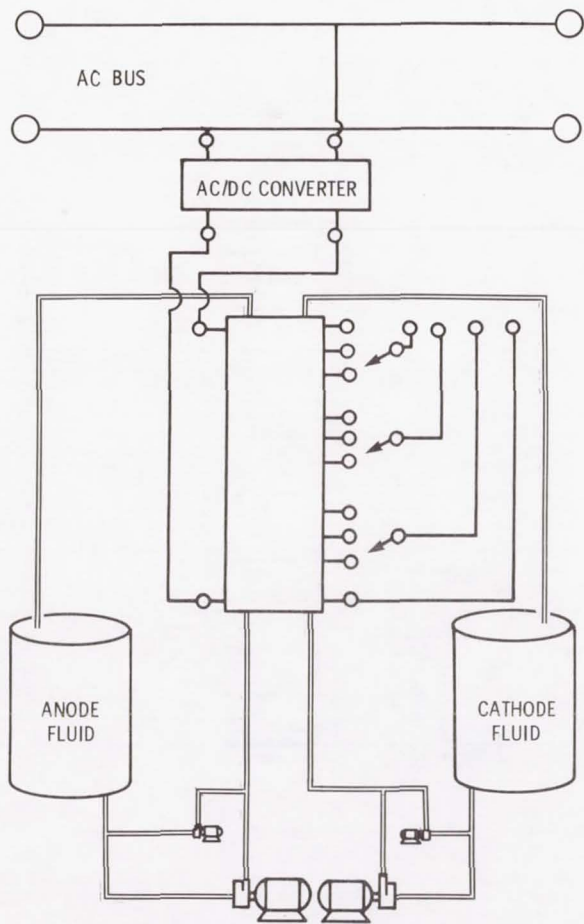


Figure 5. - Redox system as uninterruptible power supply (UPS) with multiple voltage capability.

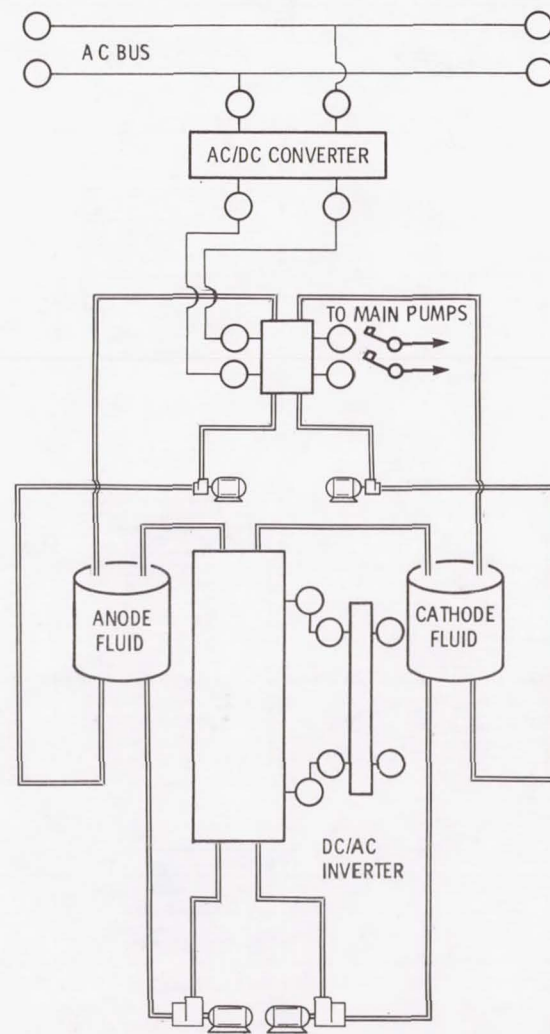
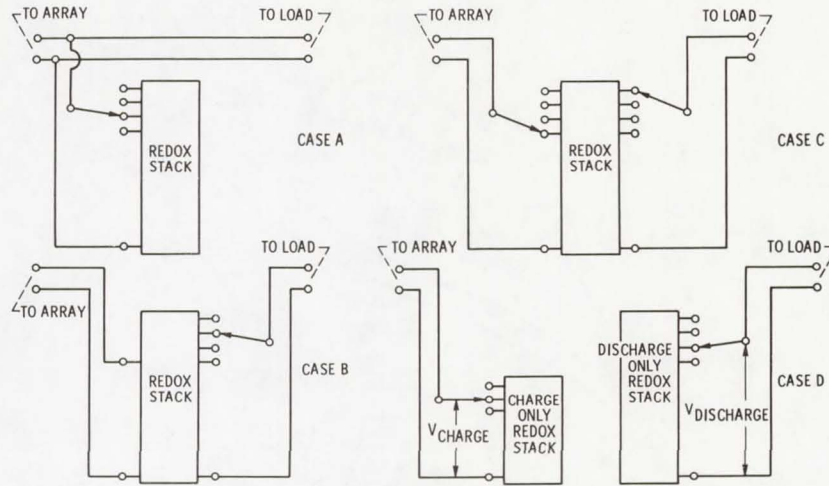


Figure 6. - Redox system as back-up power supply or as buffer between grid and load.



CASE A. REDOX STACK FLOATED ON MAIN SOLAR ARRAY BUS. CASE B. FIXED INPUT VOLTAGE AND TRIMMED OUTPUT VOLTAGE. CASE C. TRIMMED INPUT VOLTAGE AND TRIMMED OUTPUT VOLTAGE. CASE D. SEPARATE CHARGE AND DISCHARGE STACKS.

Figure 7. - Possible ways to interconnect the photovoltaic energy source to the Redox energy storage subsystem.

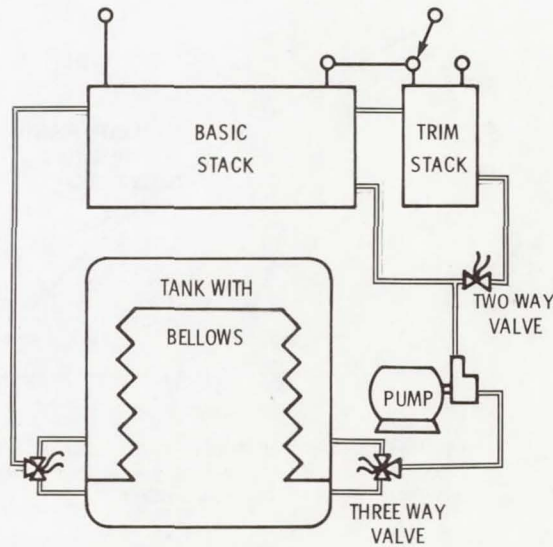


Figure 8. - Pseudo-four tank Redox system for two-pass operation.

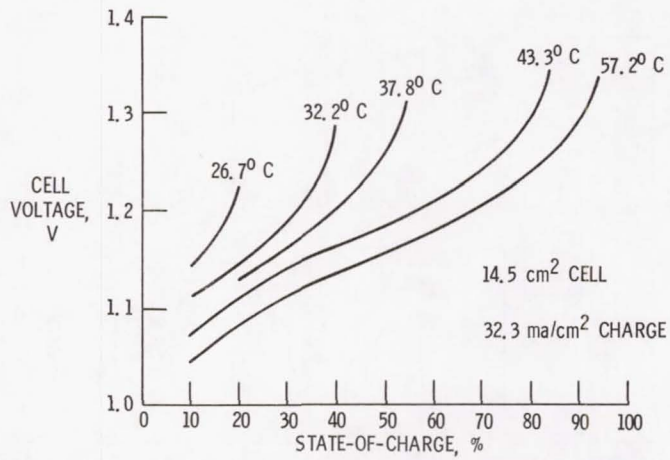


Figure 9. - Effect of temperature on constant-current charge performance of iron-chromium Redox cell.

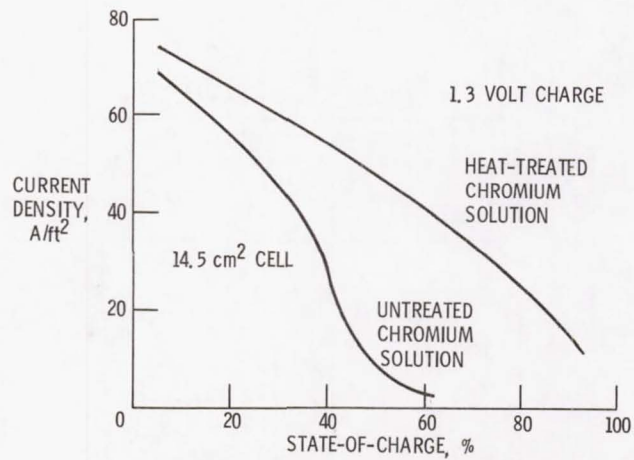


Figure 10. - Effect of heating chromium solution to 75°C, then quenching to 25°C, on charge acceptance of iron-chromium Redox cell at constant voltage.

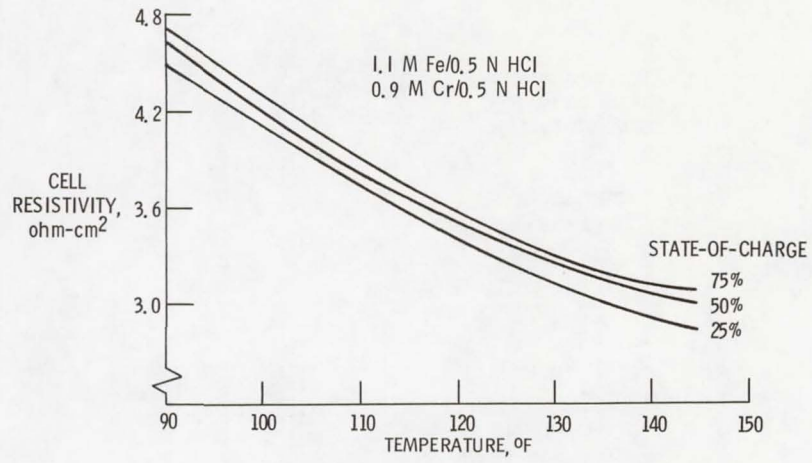


Figure 11. - Effect of temperature on Redox cell resistivity.

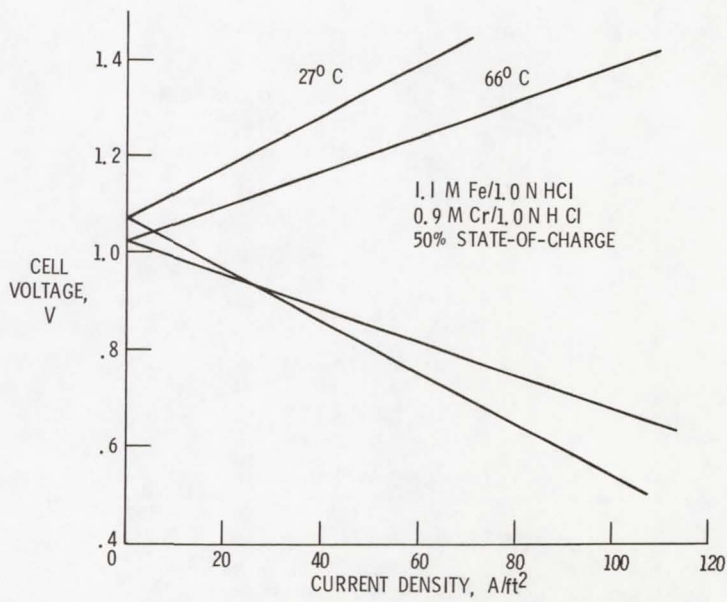


Figure 12. - Redox cell polarization curves, charge and discharge, at 27° C and 66° C.



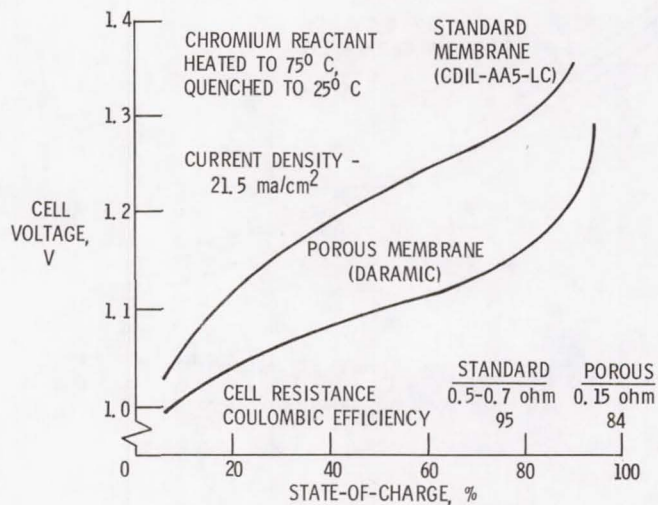


Figure 13. - Constant-current charging curves for iron-chromium cells with mixed reactants: comparison of standard ion exchange membrane and commercial, microporous separator.

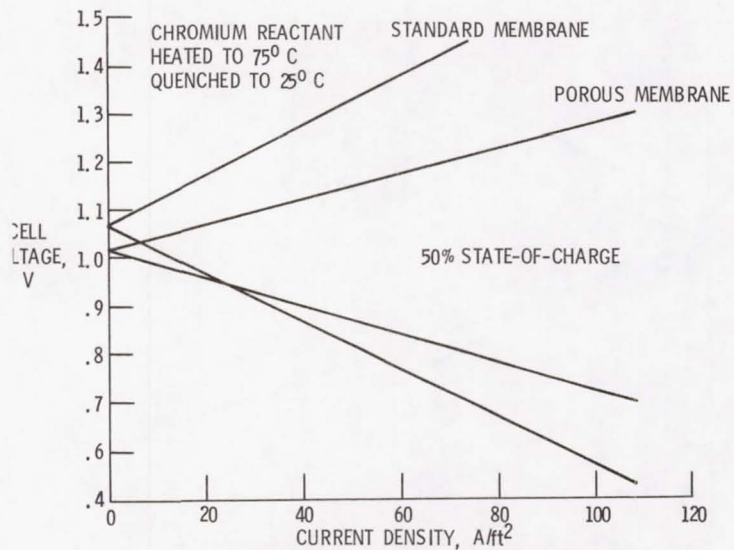


Figure 14. - Charge and discharge polarization curves for iron-chromium Redox cells: comparison of standard ion exchange membrane/separate reactants and commercial, microporous separator/mixed reactants.

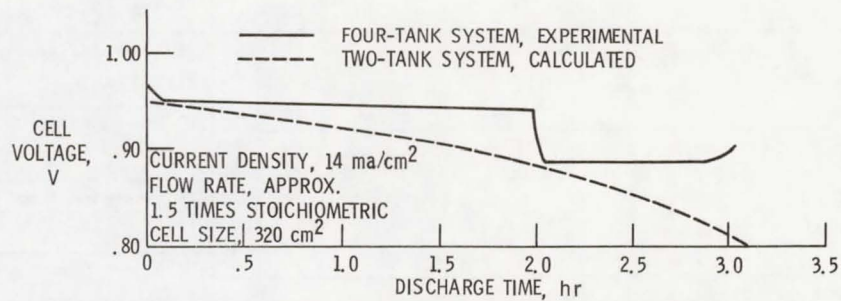


Figure 15. - Measured constant-current discharge performance of a four-tank Redox system, compared with calculated performance for a two-tank system.

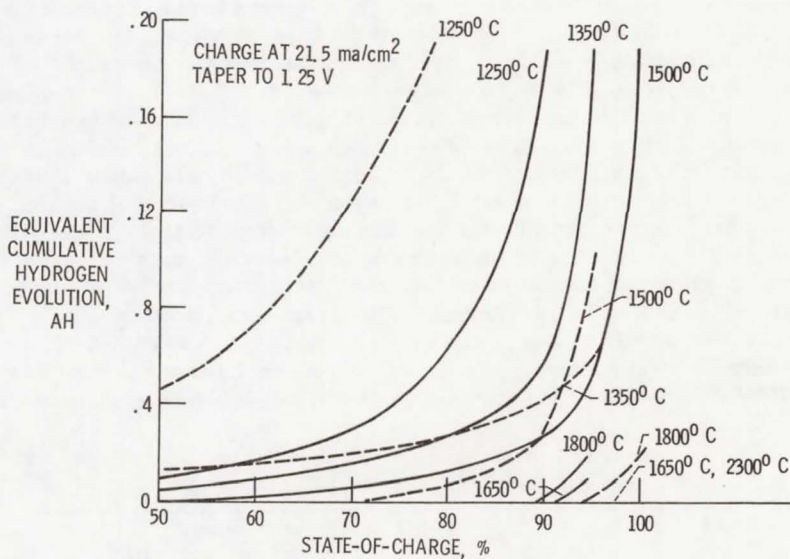


Figure 16. - Effect of felt processing temperature on the hydrogen evolution from graphitized felt chromium electrodes, during charge (solid lines, scoured felt; dashed lines, unscoured felt).

|   |  |  |            |
|---|--|--|------------|
| 1. Report No.<br>NASA TM-82854  | 2. Government Accession No.                          | 3. Recipient's Catalog No.   |            |
| 4. Title and Subtitle<br><br>DESIGN FLEXIBILITY OF REDOX FLOW SYSTEMS   |  | 5. Report Date   |            |
|   |  | 6. Performing Organization Code<br>776-72-41   |            |
| 7. Author(s)<br><br>Norman H. Hagedorn and Lawrence H. Thaller  |  | 8. Performing Organization Report No.<br>E-1223  |            |
|   |  | 10. Work Unit No.  |            |
| 9. Performing Organization Name and Address<br>National Aeronautics and Space Administration<br>Lewis Research Center<br>Cleveland, Ohio 44135  |  | 11. Contract or Grant No.  |            |
|   |  | 13. Type of Report and Period Covered<br>Technical Memorandum  |            |
| 12. Sponsoring Agency Name and Address<br>U. S. Department of Energy<br>Division of Energy Storage Systems<br>Washington, D. C. 20545   |  | 14. Sponsoring Agency Code Report No.<br>DOE/NASA/12726-16   |            |
|   |  | 15. Supplementary Notes<br>Prepared under Interagency Agreement DE-AI04-80AL12726. Prepared for Intersociety Energy Conversion Engineering Conference hosted by the Institute of Electrical and Electronics Engineers, Los Angeles, California, August 8-13, 1982. |            |
| 16. Abstract<br>The characteristics inherent in Redox flow systems permit considerable latitude in designing systems for specific storage applications. The first of these characteristics is the absence of plating/deplating reactions with their attendant morphology changes at the electrodes. This permits a given Redox system to operate over a wide range of depths-of-discharge and charge/discharge rates. The second characteristic is the separation of power generating components (stacks) from the energy storage components (tanks). This results in cost-effective system design, ease of system growth via modularization, and freedom from sizing restraints so that the whole spectrum of applications, from utilities down to single residences can be considered. The final characteristic is the commonality of the reactant fluids which assures that all cells at all times are receiving reactants at the same state-of-charge. Since no cell can be "out of balance" with respect to any other cell, it is possible for some cells to be charged while others are discharging, in effect creating a DC-to-DC transformer. It is also possible for various groups of cells to be connected to separate loads, thus supplying a range of output voltages. Also, trim cells can be used to maintain constant bus voltage as the load is changed or as the depth of discharge increases. The commonality of reactant fluids also permits any corrective measures such as rebalancing to occur at the system level instead of at the single cell level. The two parasitic or self-discharge mechanisms peculiar to flowing electrolyte systems are shunt currents and the need for pump power. These also have an impact upon the selection of suitable applications for Redox systems. Consideration is given to a number of applications, each of which takes advantage of one or more of the inherent characteristics of Redox flow systems. These various applications span a spectrum of power and energy requirements from small, uninterruptable power supplies, through stand-alone photovoltaic and wind sites to electric utility central stations. Finally, an up-date on the status of the NASA Lewis Redox system technology will be provided, focusing upon electrode and membrane developments and system cost projections. |  |  |            |
| 17. Key Words (Suggested by Author(s))<br>Flow batteries<br>Redox<br>Energy storage<br>Flow cell  |  | 18. Distribution Statement<br>Unclassified - unlimited<br>STAR Category 25<br>DOE Category UC-94cb   |            |
| 19. Security Classif. (of this report)<br>Unclassified  | 20. Security Classif. (of this page)<br>Unclassified | 21. No. of Pages   | 22. Price* |

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