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Improvement and Scale-up of the NASA Redox Storage System

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Division of Energy Storage Systems

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16. Abstract

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Abstract

As larger cells and stacks are developed and tested, the NASA Redox Energy Storage System described at the 14th IECEC meeting in August 1979 continues to show the technical performance required and cost-effectiveness for use with stand-alone photovoltaic and wind turbine installations and electric utility load-leveling. Over the past year, the anion exchange membranes and chromium electrodes have been further improved. Parametric flow studies show that pumping power requirements and shunt current losses in complete systems will be acceptable. More refined cost estimates confirm earlier predictions that system costs should be attractively low. A preprototype 1.0 kW Redox system (2 kW peak) with 11 kWh storage capacity has been built and integrated with the NASA/DOE photovoltaic test facility at NASA Lewis. This full function Redox system includes four substacks of 39 cells each (1/3 ft^2 active area) which are connected hydraulically in parallel and electrically in series. An open circuit voltage cell and a set of rebalance cells are used to continuously monitor the system state of charge and automatically maintain the anode and cathode reactants electrochemically in balance.

This paper will review recent membrane and electrode advances and briefly describe the results of multicell stack tests of 1 ft^2 hardware and the design of the 1 kW (2 kW peak) integrated system.

Introduction

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. The Redox couples currently under investigation are acidified chloride solutions of chromium (Cr^{+2}/Cr^{+3}) and iron (Fe^{+2}/Fe^{+3}). Figure 1 illustrates the system in its simplest form.

Over the past seven years, the NASA Lewis Research Center has developed the NASA Redox concept from the original idea (US Patent No. 3,996,064) to where complete Redox Energy Storage Systems have been built. The system has been described in detail in previous presentations. [1,2] Progress has been rapid in the past few years which has been recognized by the granting of an IR 100 award in 1979.

The near-term application for NASA Redox Energy Storage Systems will be small village power systems, principally in the less developed countries, where solar arrays or wind turbines would provide the power but where storage is required for night-time or periods of low sun or wind levels. The application[3] is characterized by small power requirements (5 to 25 kW) but rather long durations of dependence on the storage devices (30 to 60 hours). This type of application is ideal for Redox systems since long storage times require only expanded reactant fluid and storage tank volumes. In the remote village power system application, low life cycle cost and simplicity of operation are the major requirements. Currently, lead-acid batteries can be used but they are expensive and not easy to maintain at the system level. The NASA Redox systems promises to be inexpensive since it is constructed using relatively unsophisticated technologies, and is readily controlled and maintained due to its system level advantages. A schematic diagram of a full-function NASA Redox system is shown in Figure 2 and will be discussed in more detail below. An artist's rendition of a NASA Redox installation for photovoltaic energy storage is shown in Figure 3.

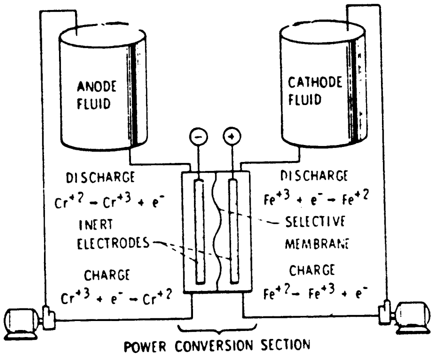

Fig. 1- Two Tank Electrically Rechargable Redox Flow Cell

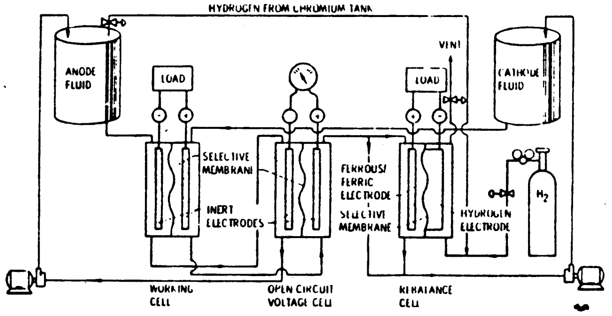

Fig. 2- Full Function Redox Flow Cell System

Another application for energy storage systems is in electric utility service where they would serve in a load leveling capacity.[4] When distributed at the interface between the transmission network and the distribution lines, these storage devices would reasonably be in the ten megewatt 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 important candidate for this service.

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A full-function NASA Redox Energy Storage System as pictured in Figure 2 includes a cell stack of the desired power output. An open-circuit voltage cell not placed under load serves to indicate the state of charge of the system as given by the Nernst equation:

$$E = 1.075 - 0.059 \log [Cr^{+3}][Fe^{+2}]/[Cr^{+2}][Fe^{+3}].$$

A plot of the calculated open circuit voltage vs. depth of discharge is given in Figure 4.

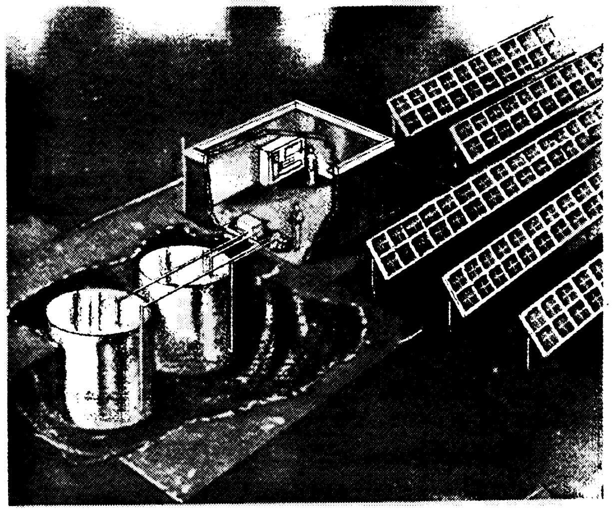

Fig. 3- NASA Redox Installation for Photovoltaic Energy Storage

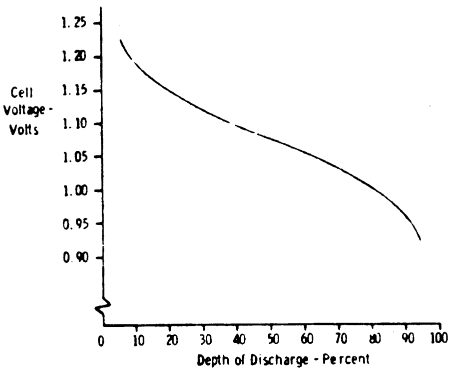

Fig. 4- Open Circuit Voltage of an Iron-Chromium Redox Cell as a Function of Depth of Discharge

Since the individual cell voltage varies with depth of discharge, additional cells called "trim cells" can be utilized to keep the stack voltage within a narrow band. These can be switched in and out as needed when the stack voltage rises or falls and the depth of discharge varies.

The other major component of the full function system is the rebalance cell, which serves to keep the two reactants at the same state of charge. An inbalance can occur due to one or more of the following reactions:(1) coevolution of hydrogen along with reduction of Cr^{+3} during charge,(2) chemical reduction of hydrogen ions by chromous ions, or (3) air intrusion into the system causing oxidation of chromous or ferrous ions. The first of these is the most important and causes a small excess of Fe^{+3} over Cr^{+2} at the end of the charging cycle. If not corrected, this imbalance increases with cycling, leading to an ever-increasing loss of capacity of the system. In the rebalance cell, the accumulated hydrogen is oxidized at a hydrogen electrode, at the same time reducing the excess Fe^{+3} at a Redox electrode. Occasional externally supplied hydrogen is needed due to unavoidable losses of small amounts of the coevolved hydrogen. The open-circuit voltage cell and the rebalance cell can be separate entities as in laboratory systems or be combined in a stack with the working cells. In such a stack the anode and cathode fluids are shared in common with all the cells so that all cells including trim cells are at the same state of charge as monitored by the open-circuit voltage cell. A single rebalance cell is sufficient to keep many working cells in balance. The only additional components needed are tanks for fluid storage, pumps, and suitable controls. A number of full-function stacks and systems have been built and tested.

This paper will describe the most recent developments in the following areas:

1. Advances in Redox technology including membranes, electrodes, and flow studies.

2. Scale-up of hardware to 1 ft^2.

3. Construction of the 1 kW preprototype Redox system and its integration with the NASA/DOE LeRC Photovoltaic Systems Test Facility.

4. Systems cost projections.

Advances in NASA Redox Technology

Membranes. One fundamental requirement for a Redox system is an ion-exchange membrane of high resistance to cross-diffusion of the reactive cations (selectivity) combined with high conductivity for the H^+ and Cl^- current-carrying ions. Ion-exchange membranes used in the NASA Redox system have been developed under contract by Ionics, Inc. of Watertown, MA.[5] Selectivity has been steadily improved over the past six years and resistivity reduced. A typical cross-diffusion rate (selectivity) of a "good" membrane is 20 $\mu g/hr/cm^2/M/L$ after 1000 hours in a Redox cell. Area resistivity in an operating Redox cell averages 5-5.5 Ω-cm^2. This selectivity is adequate for photovoltaic applications, which are characterized by high reactant volume to membrane areas, and the resistivity already meets the anticipated requirements.

Improvements of about three-fold are needed in both areas for the more demanding utility load-leveling applications. During the past year changes in catalyst level and inert (non-polymerizable) content reduced the resistance of the membrane by about 30%. Since the voltage losses in the cell are almost entirely due to the IR drop in the membrane, this means that a 30% greater current density can now be achieved at the same voltage levels. This results in a lower cost for the stored energy. Figure 5 shows a polarization curve for a cell with one of the newer membranes.

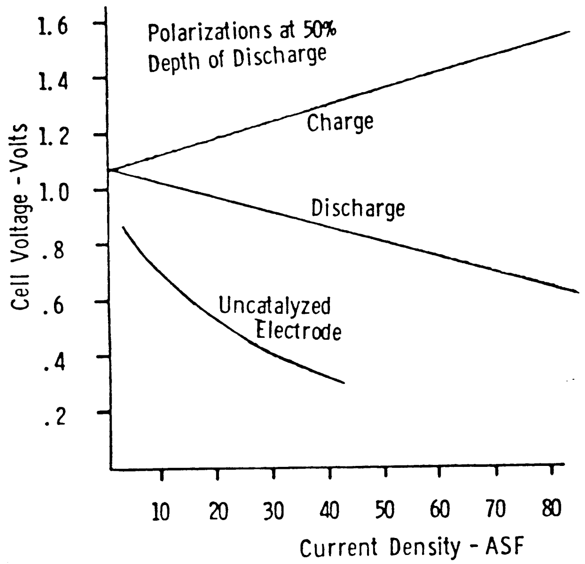

Fig. 5- Performance of 0.33 ft^2 Single Cell With Best Membrane and Electrodes

Electrodes. The requirement of rapid rates of the electrode reactions is met satisfactorily on the iron side by having electrodes of bare carbon felt, but a catalyst is needed on the chromium side to increase the rate of chromium reduction. The catalyst must also have a high overvoltage for hydrogen. Thermodynamically, hydrogen is evolved before chromium is reduced. Appreciable coevolution of hydrogen not only reduces the current efficiency of the system but over the course of many cycles allows the system to get out of balance and thus lose effective capacity. Giner, Inc. of Waltham, MA[6] found under contract that trace amounts of gold and lead (12-25 μg/Au/cm^2 and 100-200 μg Pb/cm^2) would meet these requirements. Lead metal has long been known as an effective catalyst for the reduction of Cr^{+3}. The presence of trace amounts of Au seems to be necessary to produce a surface on which the Pb plates (or adsorbs) uniformly during the charging cycle. The Au-Pb catalyst also improves the discharge rate of the cell.

In scaling up the NASA Redox system, a new lot of carbon felt was purchased from the vendor, Fiber Materials, Inc. of Biddeford, ME. This is produced by thermal decomposition of 1/8" rayon felt. Final thickness of most samples is in the range of 0.080-0.090". It was found that electrodes prepared with this new lot had much higher rates of hydrogen evolution than those made with the original lot as well as poor voltages on discharge (Figure 6). Discussions with the manufacturer did not reveal any obvious reasons for this behavior. The only significant difference observed between lots of felt was the wettability. An extensive program was carried out to characterize the felts and to find a "normalization" procedure which would produce satisfactory electrodes from any lot of felt. This program has been described in detail elsewhere.[7] As a result of this effort, a new method of pretreatment and deposition of the gold has produced electrodes which do not evolve measurable amounts of hydrogen until the cell is more than 95% fully charged. In addition, these electrodes show excellent performance on discharge. These procedures seem entirely adequate for small cells and large single cells. Whether further refinements will be needed for electrodes for large stacks will be determined as scale-up proceeds.

Flow Studies. During the past year more exhaustive studies have been made of the trade-offs between shunt currents, pumping power, and cell performance. Figure 7 shows the overall view of a NASA Redox stack with an exploded view of a single cell. Figure 8 shows the flow plate and electrode used in the standard 0.33 ft^2 cell. In this cell configuration narrow inlet and outlet slits connect the main manifolds to the secondary manifolds at the base of the electrodes. The secondary manifold allows the incoming liquid to spread out along the width of the electrode prior to its flow through the carbon felt electrode placed in the cavity between the membranes and the bipolar plate. This flow proceeds from the bottom of the cell up to the top where another secondary manifold connects through the exit port to the exit manifold.

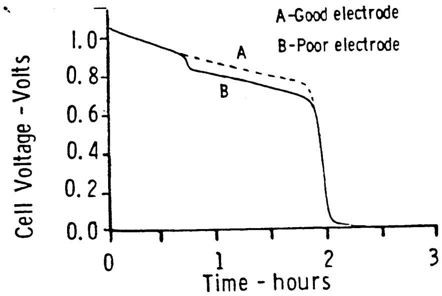

Fig. 6- Effect of Electrode Catalyst on Discharge Performance

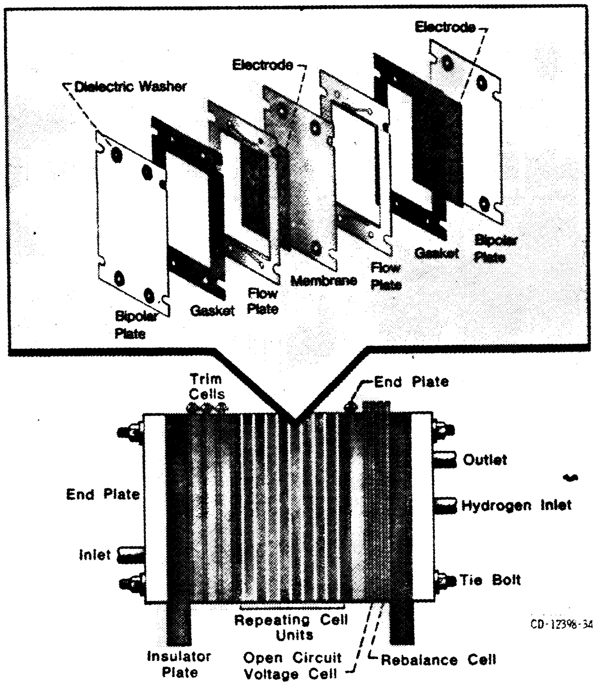

Fig. 7- Redox Stack and Single Cell Components

Obviously pumping losses can be reduced by operating at low flow rates. However, at very low flow rates, the reactants may be sufficiently de-

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pleted before they leave the cell so that a reduction in the cell voltage takes place due to a Nernstian correction (log $[Cr^{+3}]/[Cr^{+2}] \times [Fe^{+2}]/[Fe^{+3}]$. At such low rates and concentrations there may also be diffusion limitations and kinetic polarization.

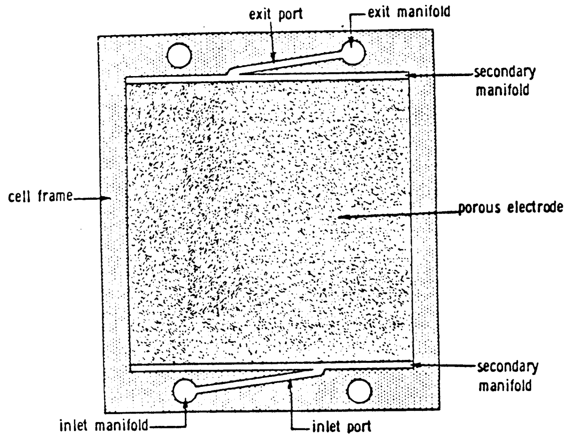


Fig. 8- Planform of Cell Using Porous Flow-thru Electrode

The stoichiometric flow rate (SFR) is defined as that flow rate at which the reactants are fully depleted just as they reach the end of the cell and is obviously the lowest flow rate at which the cell can operate. The SFR is a function of the solution concentration, the fractional state of charge (FSC), and the current drawn by the cell. This is given by the equation SFR = I/1.608 FSC for 1.0 M solutions where I is in amps and the SFR is in cm^3/min. In Figure 9 a performance map is shown for a 1 ft^2 cell at 50% FSC at various flow rates. It can be seen that the minimum flow rate needed in practice for good performance is 1.5 x SFR. Studies at other depths of discharge give similar results. Calculations show that the polarization above this flow rate can be accounted for by IR losses and Nernstian corrections. At a flow rate of 1.5 x SFR and below, diffusion and kinetic polarizations become significant.

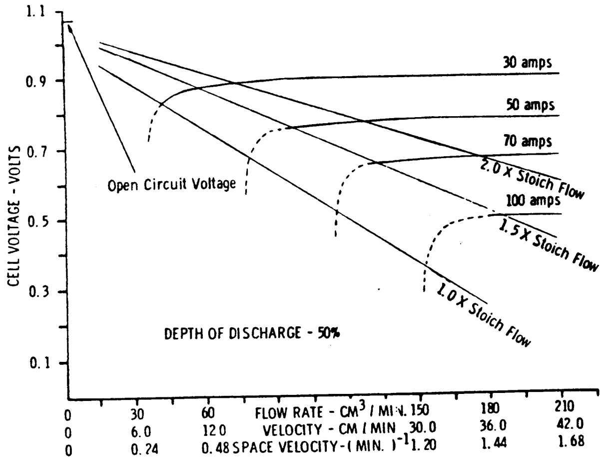


Fig. 9- Performance Map of a One Ft^2 Single Cell

Pumping power losses can also be decreased by increasing the width and depth and reducing the length of the inlet and exit ports. However, these same changes increase the shunt power losses in a stack, so that the trade-offs between the two must be considered. Using a model developed earlier,[8] the shunt losses per stack can be calculated as a function of the number of cells in the stack and the resistance across the cell from inlet manifold to exit manifold (Figure 10). The predictions of this model are confirmed by experience with stacks, provided that the ionically conductive membranes and electronically conductive bipolar plates are insulated from the manifolds to reduce shunt paths.

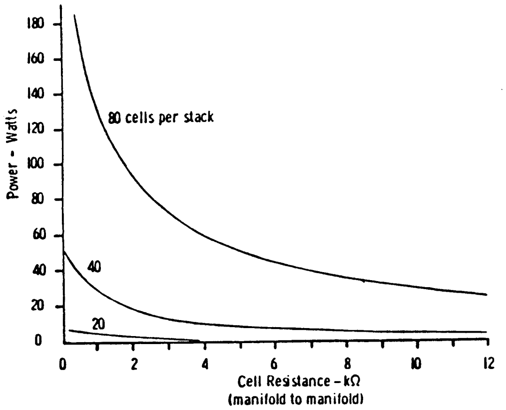
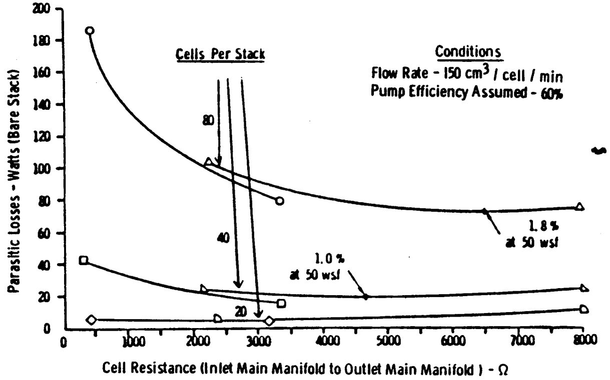


Fig. 10- Shunt Losses per Stack as Predicted by NASA Model

From measurements of pressure drops at various flow rates, ideal pump power losses can be calculated and the combined shunt and pump power losses computed for various cases. Figure 11 shows an example of some of these calculations for a 1 ft^2 cell. The numerical losses in watts are relatively independent of cell size, but the percentage loss depends on the cell size and the current density. Thus the percentage loss in a 0.33 ft^2 cell under the same conditions as the 1 ft^2 cell would be three times as great. The losses are also very dependent on pump efficiency, especially as the cell resistance increases. Unfortunately, efficient pumps are not presently available in small sizes. It is possible that a development effort in this direction may become desirable in the future. Ultimately the most desirable cell and stack configuration will depend on many factors and would have to be determined for each case. For a properly designed system the parasitic losses should not exceed a few percent.



Note: calculations do not include stack to stack shunt losses or pumping losses outside of stacks.

Fig. 11- Calculated Sum of Shunt Power and Pump Power for Flow Cell Stacks

1 Ft^2 Hardware. The flow studies have shown that hardware of about 1 ft^2 active area is an advantageous size for the 10 kW system planned as the next step in NASA Redox development. A number of cells of this size have been built and tested. Cycling studies and flow studies have shown the predicted performance. As of the time of this writing, a five cell stack that included an open circuit voltage cell has also been tested satisfactorily. This hardware size is probably adequate for most photovoltaic and wind storage applications. For the megwatt utility load leveling applications, 5-6 ft^2 hardware is envisioned.

System Cost Analysis. A recent update of NASA Redox system costs was carried out under contract by the Power Systems Division of United Technologies, Inc. This study addressed the probable FOB selling price of complete NASA Redox systems of either a 10 kW-500 kWhr size or a 10 MV-100 MW hour size. The similarity between Redox stack hardware and fuel cell hardware is obvious, and UTC has developed an extensive background in developing estimates for this class of equipment. The first round of estimates have been completed and identified the tankage as one of the major cost centers.

In general, this study confirmed earlier estimates in terms of the relative significance of the storage-related and power-related portions of the overall system. The impact of the flow rate selection became very apparent as it relates to the overall system efficiency. In-house performance mapping studies revealed that a higher than required flow rate was selected for the initial system design and configuration parameters. A second iteration of the cost studies using these later results will result in a conceptual system design that is a closer reflection of the actual flow requirements. Current system cost estimates are in the range of \$40-\$60/kWhr for a complete 10 kW-500 kWhr system (vs. \$150/kWhr for Pb-Acid cells). The 10 MW-100 MWhr system is expected to be somewhat less but the results are not yet as firm.

1 kW Preprototype NASA Redox System. At the time of this writing, all stacks of the preprototype 1 kW Redox system are completed and the full system is assembled. This system consists of four substacks connected hydraulically in parallel and electrically in series. Design information is given in Table 1. The four stacks are shown in Figure 12. In addition to the information gained by the 10-fold scale-up over previous systems, information will also be obtained on the performance of the NASA Redox system when mated with a photovoltaic system, charging in a random manner dependent on the solar power available and discharging in a random manner dependent on the load. Information will also be obtained on how best to electrically interconnect the photovoltaic array, Redox system, and load in such a system. A discussion of the various methods of interconnection is included in a recent publication.[9]

Conclusion

NASA Redox system technology has advanced considerably in the past year to the point where a complete 1 kW preprototype system is being integrated and tested with the DOE/NASA Lewis Solar Photovoltaic Test Facility. This test should provide design information and practical operating experience useful for the 10 kW systems now planned. Scale-up of hardware has presented no major problems. The effects of a wider range of temperatures still needs to be explored further, as do the effects of possible impurities in commercial chemicals, osmotic effects, and the use of higher concentrations of reagents. The biggest technical problem is still seen as the membrane resistivity which is adequate for photovoltaic storage applications but needs to be at least halved for load-leveling use.

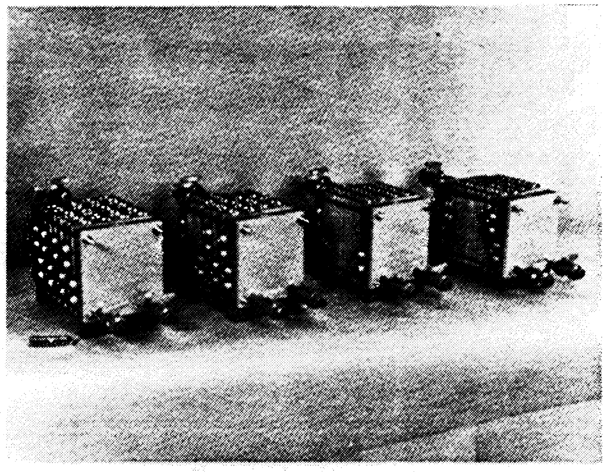


Fig. 12- Four Stacks of 1.0 kW Preprototype NASA Lewis Redox Storage System

As more and larger systems are built and tested, the cost and systems advantages of the NASA Redox system should become more apparent.

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Table 1 Redox System Design Parameters

Gross Power	1260 watts
Nominal Net Power	1000 watts
Voltage	120 ± 5%, VDC
Number of Stacks	4
Number of Cells/Stack	39
Trim Packages	10 packages, 6 cells each
Depth of Discharge Range (Utilization)	80%-20% (0.60)
Reactant Volume (Each)	700ℓ (186 U.S. gallons)
Reactant Energy Density	14.5 Wh/ℓ (End of Life)
Cell Active Area	320 cm^2
Nominal Current Density	30 ma/cm^2
Reactants	1M/ℓ $FeCl_3$, 2N HCl 1M/ℓ $CrCl_2$, 2N HCl
Reactant Flow Rates (Nominal)	100-150 cm^3/min-cell
Parasitic Losses	Pumps-200 watts (15% pump efficiency) Shunt Power Losses - 125 watt
Number of Rebalance Cells	5
Number of Charge-Indicator Cells	1