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NASA Redox System Development Project Status

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



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NASA REDOX STORAGE SYSTEM PROJECT STATUS

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Abstract

E-939 NASA-Redox energy storage systems are being developed for solar power applications and utility load leveling applications by the Lewis Research Center for the Department of Energy. The major objective of the project is to establish the technology readiness of Redox energy storage for transfer to industry for product development and commercialization by industry.

The approach is to competitively contract to design, build and test Redox systems progressively from preprototype to prototype multiKW and megawatt systems and conduct supporting technology advancement tasks.

The Redox electrode and membrane have been shown to be fully adequate for multiKW solar related applications and the viability of the Redox system technology has been demonstrated for multiKW solar related applications.

The status of the NASA Redox Storage System Project will be described along with the goals and objectives of the project elements.

Introduction

As part of the Department of Energy (DOE) electrochemical storage effort, the Lewis Research Center (LeRC) of the National Aeronautics and Space Administration (NASA), under DOE-NASA Interagency Agreement DE-AI04-80AL1276, is carrying out the NASA Redox Storage System Development Project. The DOE Office of Advanced Conservation Technologies is responsible for formulating and managing research and development in energy storage technology. Major responsibility for program management has been shifted to the DOE national laboratories and, therefore, the Sandia National Laboratories (SNL) in Albuquerque, New Mexico has been assigned responsibility for program management of Redox activities. SNL has been delegated this responsibility through the DOE Albuquerque Operations Office (ALO).

An ERDA approved Project Development Plan entitled "Redox Flow Cell Development and Demonstration Plan" dated December 14, 1974 described a phased effort to develop and demonstrate a NASA conceived Redox flow system at sufficient energy storage capacity to provide useful operational and preliminary cost data as the basic input for the design and construction of systems for commercial applications. In the succeeding years, with complementary support from NASA, the Redox technology has advanced to the point that the enabling technologies of ion exchange membranes and electrocatalysts have demonstrated their adequacy for solar related storage applications. Further, a series of system related concepts have been added to the basic concept and technical feasibility demonstrated in a fully integrated 1 kW Redox system.

Objectives

The overall objectives of the NASA Redox Storage System Development Project are to develop and demonstrate the technology readiness of the NASA

Redox system for both solar related applications and utility load leveling applications and to achieve Redox technology transfer to industry for product development and commercialization by industry. Major project goals to achieve the objectives include completion of a multi-kW prototype system field test of a solar storage application and to provide a megawatt storage system, ready for test in the DOE/EPRI Battery Energy Storage Test facility. The project's activities will be accomplished principally through competitive contracts with the private sector. The primary contractual effort is planned to be an integrated task which takes Redox through the evolutionary stages related to development and demonstration of technology readiness. Government funds in support of this project will be provided by DOE.

Technical Accomplishments

Significant progress has been made at the component, subsystem and system levels in the development of Redox technology. Both membrane resistivity and selectivity have been shown to be adequate for solar related applications. However, further improvements are possible and such improvements will continue to be investigated. Figure 1 illustrates the progress made in advancing from laboratory size membranes to complete systems.

Membrane technology advances have demonstrated steady progress in size scaleup and yield rate of quality membrane formulations along with an increasing understanding of ferric ion fouling, water transfer, and membrane quality requirements. Membrane resistivity has been reduced from $7.0 \Omega\text{-cm}^2$ (Sept. 1978) to the present level of $3.6 \Omega\text{-cm}^2$. The goals are $3.0 \Omega\text{-cm}^2$ for solar related applications and $1.5 \Omega\text{-cm}^2$ for utility load leveling applications. Membrane selectivity of $18 \mu\text{gm/hr/cm}^2/\text{M/L}$ has been achieved. The goal is $15 \mu\text{gm/hr/cm}^2/\text{M/L}$ for solar related applications and $5 \mu\text{gm/hr/cm}^2/\text{M/L}$ for utility applications. These improvements have been reported in detail in Refs. 1 and 2.

Electrode technology has shown significant improvement. Present laboratory cells have demonstrated excellent catalyst stability and have exceeded cycling goals by a substantial margin with a performance loss of less than 5% after cyclic operation equivalent to over 50 years of daily cycles. The current lead/gold catalyst formulations have been shown to be fully adequate in all respects. References 3 and 4 provide additional electrode information. Single cell performance continues to improve. Present cells have achieved a peak power density of 100 watts/ft^2 as shown in Fig. 2.

Testing of cells as short stacks has yielded watt-hour, round trip efficiencies of 81% at 20 amps/ft^2 and coulombic efficiencies of 98%.

Shunt currents have been reduced significantly since 1978 as illustrated in Fig. 3 and are very near to values predicted by the LeRC shunt current model (Ref. 8).

A 1 kW Preprototype Redox storage system has been designed and built and is in operation as a test bed for evaluating the interaction of a complete, full function, Redox system with a photovoltaic array (NASA/LeRC/DOE Systems Test Facility).

The 1 kW Preprototype Redox system is shown in Fig. 4. The system will supply 1 kW nominal at a current density of 30 amps/ft^2 . For test convenience storage capability was limited to 12 kWh. The system consists of 4 stacks with a total of 156 active cells. The status of Redox system technology development is summarized in Table 1, with qualitative designation of the level of technical improvement (small, medium, large) needed for the two

major application scenarios. The cost of chromium chloride is the subject of current study and is uncertain at this time for the large systems.

Project Overview

Figure 5 displays, in summary form, the major project elements. The schedule reflects the revisions made necessary by the recent budget reductions for 1981 and 1982. Each element is described in more detail below.

Deferral of award of a multi-kW system development contract until at least 1982 delays entry of Redox system technology into the industrial sector by at least one year. Planned Application analyses tasks have been deferred until 1983, however, supporting technology tasks will continue at the planned level to permit continued improvement in membranes, electrodes and component level designs.

Prototype Systems Development

A contract for the evolutionary development of Redox systems is viewed as an instrument to enable the transfer of Redox technology from the government laboratory to the private sector. To date, all Redox system technology development has been performed at the Lewis Research Center (LeRC). Papers have been published and an Industry Briefing was held at LeRC in July 1980 to initiate the technology transfer process. This has been followed by an open door policy for interested companies. However, the design, building and testing of systems by the industry is necessary to effect a meaningful transfer of technology. Prototype systems development has as its primary focus the implementation of a multi-year contractual effort to design, build, test and establish the technical and economic viability of Redox systems for a variety of applications such as the artist's concepts shown in Figs. 6 and 7. The procurement would initiate a phased approach to achieving the transfer of Redox technology to industry for eventual commercialization by industry. To date, the only direct industrial involvement with the NASA Lewis Redox Project has been research and technology in the areas of membranes and electrodes by Ionics, Inc. and Giner, Inc., respectively and in the supply of graphite and carbon bi-polar plates by several companies.

Initially, the procurement would encompass the design, fabrication and test of preprototype multi-kW systems; a conceptual megawatt Redox system design and the conceptual design of a 100 kW sub-module as the basic modular element of the megawatt system. Based on the results of these activities, a decision will be made whether or not to initiate the prototype development of Redox systems. This development would include the design, fabrication and test of prototype multi-kW systems; the design fabrication and test of a 100 kW module and the design and fabrication of a megawatt system for test in the BEST facility. The testing of these systems in realistic environments would prove the technical and economic viability of Redox storage and provide the operating experience needed for further system improvement.

To support the system development activity a 1 kW Preprototype System was designed and fabricated at the LeRC and testing initiated during 1980. The system is illustrated in Fig. 4. A block diagram of the system is shown in Fig. 8 and the nominal design specifications are tabulated in Table 2.

The first system tests focused on characterizing the performance of the system and consisted of polarization tests, charge/discharge cycles and performance vs. flow rate measurements. In these tests all 156 cells were active and system charging was done with a DC power supply. Pumps,

instruments and controls were also powered externally. A later test was performed with the Redox system coupled to a 5 kW photovoltaic array providing power to a resistive load bank. These tests provided much valuable information. Control concepts were shown to be valid and trouble free, insight was gained in the interaction between the Redox system, pv array and load interfaces. Quantitative data on the loss mechanisms in the system have given direction for stack and system design changes to minimize these losses. Overall, the system performed well. These system tests are reported in detail in Ref. 5. Additional system related design requirements are discussed in Ref. 6.

Application Analyses

Specific activities have been completed or are planned to provide conceptual designs of Redox storage system applications in sufficient depth to identify operational characteristics and permit credible application cost projections. Institutional issues related to Redox system deployment and technology transfer are being addressed. Redox storage system conceptual designs have been established to estimate production cost and determine the influence of various parameters on production cost. In order to assist in specifying a minimum cost system for a given power and energy storage requirement, a computer program has been prepared which determines a value of current density corresponding to a minimum system cost. This value of current density is then utilized to compute many other design variables. A Redox cost projection study has been recently completed under contract by United Technology Corporation (Ref. 7). The results of the study are shown in Tables 3 and 4 and are for the following cases:

10 kW/500 kWh Redox systems at an annual production rate of 1000 units

10 mW/100 mWh Redox systems at an annual production rate of 100 units

A significant conclusion drawn from the study is that the Redox cell and stack are amenable to mass production techniques with a relatively low material cost. In both cases, the system cost is dominated by the cost of the reactants and associated tankage. Lower costs for the megawatt systems are largely due to a current density of 100 amps/ft² as opposed to 50 amp/ft² for the multikW systems, a much higher production volume of components for the megawatt systems and a reactant concentration of 2 molar. Figure 9 indicates the relationship between specific cost and storage duration based on the study results.

A preliminary assessment of the market penetration potential for residential Redox system applications has been completed. The approach was to perform a financial analysis of a 5 kW/25 kWh Redox system in a favorable residential application and compare with grid only and advanced lead acid battery storage. Table 5 indicates some of the study assumptions and Table 6 summarizes the results. The major conclusion to be drawn from these results is that the projected economics of these storage systems are not conducive to stimulating near term applications.

Application concept studies originally planned to begin in late 1981 and 1982 have been deferred until 1983. These concepts will be generated for residential, commercial, industrial and solar stand-alone applications. These data will then be used as the basis for detailed cost evaluations.

Since the cost of reactant is a significant portion of the total system cost, methods for reducing the costs of the reactant processing will be investigated. At present, potential low cost production methods for chromic chloride have not been implemented due to the current low demand. With the increased demand that would be created by a viable Redox storage system industry and the co-requirement for ferrous chloride, a dedicated Redox reactant solution manufacturing, and solution refurbishment capability would afford major cost reductions directly applicable to Redox system costs.

Supporting Technology

Membranes

During the past year, membrane R&D activity was focused on optimizing the chemical formulations for area resistivity and selectivity and to improve fabrication techniques to obtain higher yield and progress to larger size membranes. Single cell components comprising stacks including the membranes are shown in Fig. 10. Membranes which perform well in selectivity and resistivity screening tests are then tested in small Redox cells. Results of performance testing are shown in Fig. 11.

The improvement in discharge current density at 0.9 volt is about 43%. However, further improvements are under investigation. A similar set of data was obtained using a new, thin fabric membrane. The results shown in Fig. 12 are promising. An improvement of about 16% is indicated over the present membranes, however, the selectivity of this membrane is not as good. Further testing is in progress to increase the selectivity while maintaining the improved area resistivity. Other investigations are in progress related to performance of membranes in 1.5 molar solutions, water transfer, temperature limits and improvements in the reactions associated with other chromium ion species existing in the solutions.

Electrodes

Redox flow cell performance is largely determined by the electrochemical characteristics of the inert electrodes. The electrode is also shown in Fig. 10. The requirement for a reversible iron electrode has been met satisfactorily using an uncatalyzed carbon felt. For the chromium electrode, however, a lead-gold catalyst is needed to increase the rates of chromium reduction and oxidation and to provide a hydrogen evolution overpotential. Appreciable co-evolution of hydrogen not only reduces the current efficiency of the system but, over a period of many cycles allows the system reactants to become chemically out of balance which leads to loss of storage capacity. However, significant improvements have been achieved in electrode performance as shown in Fig. 13.

The addition of the NASA Lewis developed rebalance cell serves to keep the two reactants at the same state of charge, thus offsetting the adverse effects of small amounts of H₂ evolution. 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 co-evolved hydrogen. A single rebalance cell is sufficient to keep many working cells in balance without any interruption in system operation.

The performance of the carbon felt electrode depends on the production history of the felt, the cleaning procedure and surface activation treatment and the methods of gold and lead deposition.

One of the main issues in the chromium electrode development work is to consistently prepare electrodes with good electrochemical performance. Variations in carbon felt properties from lot to lot and within a lot, appear to account for most of the variations in performance. Specific cleaning treatments and catalyzation procedures can generally be identified for each lot of carbon felt. However, a "normalization" step for all lots of felt has not yet been developed. An activity is in progress with the carbon felt manufacturer to systematically identify a carbon felt fabrication procedure to manufacture "Redox grade" carbon felt.

Conclusion

The technical feasibility of the NASA-Redox storage concept has been established. Present performance characteristics appear fully adequate to meet the requirements of solar related applications. Utility load leveling applications require improvements in membrane technology, namely reduction in area resistivity and higher selectivity. It remains to translate the existing technology into larger systems in a realistic operational environment to obtain interface and operational data as input to the design and test of prototype systems.

References

1. Ling, J. S.; Charleston, J. Advances in Membrane Technology for the NASA Redox Energy Storage System. NASA Lewis Research Center, Cleveland, Ohio. Presented at the 1980 Meeting of the Electrochemical Society, Oct. 5-10, 1980.
2. Reid, M. A.; Thaller, L. H. Improvement and Scaleup of the NASA Redox Storage System. NASA Lewis Research Center, Cleveland, Ohio, DOE/NASA 12726-6, NASA TM 81632.
3. Gahn, R. F.; Charleston, J.; Ling, J. S.; Reid, M. A., Performance of Advanced Chromium Electrodes for the NASA Redox Energy Storage System. NASA Lewis Research Center, Cleveland, Ohio. Presented at the Electrochemical Society Meeting, Oct. 5-10, 1980.
4. Reid, M. A.; Gahn, R. F.; Ling, J. S.; Charleston, J. Preparation and Characterization of Electrodes for the NASA Redox Storage System. NASA Lewis Research Center, Cleveland, Ohio. Prepared for the Journal of Electrochemical Society.
5. Hagedorn, N. H., The NASA Preprototype Redox Storage System for a Photovoltaic Stand-Alone Application. NASA Lewis Research Center, Cleveland, Ohio. For presentation at the 1981 16th IECEC Conference, Atlanta, GA, August 9-14, 1981. DOE/NASA 12726-8 NASA TM-82607.
6. Hagedorn, N. H.; Thaller, L. H. Redox Storage Systems for Solar Applications. NASA Lewis Research Center, Cleveland, Ohio. DOE/NASA 1002-80/5, NASA TM 81464.
7. Stedman, J. K.; Michaels, K. B.; Hall, E. W., Cost Projections for Redox Energy Storage Systems-Final Report. United Technologies Corp., South Windsor, Connecticut. DOE/NASA 01264, NASA CR 165260.
8. Prokopius, P. R., Model for Calculating Electrolytic Shunt Path Losses in Large Electrochemical Energy Conversion Systems. NASA Lewis Research Center, Cleveland, Ohio, NASA TM X-3359.

TABLE 1. - SUMMARY REDOX SYSTEM DEVELOPMENT

Factor	Satisfactory for multiKW solar applications	Satisfactory for multiMW utility applications	Improvement needed (small-S) (medium-M) (large-L)
1. Membranes	Yes	No	S
2. Electrodes	Yes	Yes	-
3. Shunt currents	Yes	Yes	-
4. Pump efficiency	No	Yes	M
5. Chromium chloride			
-cost	Yes	?	?
-availability	Yes	No	M
6. Reactant tankage	Yes	No	M
7. Manufacturability	Yes	Yes	-

TABLE 2. - DESIGN INFORMATION ON 1.0 kW REDOX SYSTEM

Power out - 1.0 kW nominal (30 ASF), 2 kW peak (65 ASF)
Voltage - 120 V D.C. \pm 5% (using trim cell regulation)
Typical single cell voltage (OCV) - 1.18 V (10% DOD) - 0.94 V (90% DOD)
System capacity - 13 kW hr (10% + 90% DOD, beginning of life)
Tank volume - 200 gallons per reactant (10% ullage)
Configuration - 4 substacks hydraulically in parallel and electrically in series
Typical substack - 39 single cells - 14" long
Trims substack - 6 sets of 6 - cell trim packages, one (1) 3-cell trim package - 1 open circuit voltage cell
Cell size - 9"x10" overall (0.33 ft ² active area)

TABLE 3. - MANUFACTURER'S SELLING PRICE -

10 kW/500 kWh REDOX SYSTEM

(Annual Production Rate = 1000 units)

Reactant Concentration = 1 molar

Cell stack	\$367.56/kW	} (1)
BOS, ^a tanks, chemicals	68.03/kWh	
Cell stack	\$363.10/kW	} (2)
BOS, ^a tanks, chemicals	109.91/kWh	
The range reflects the chromic reactant cost range from (1) \$0.32/lb to (2) \$1.30/lb.		

^aBalance of system.

TABLE 4. - MANUFACTURER'S SELLING PRICE -

10 MW/100 MWh REDOX SYSTEM

(Annual Production Rate = 100 units)

Reactant Concentration = 2 molar

Cell stack	\$136.59/kW	} (1)
BOS, ^a tanks, chemicals	54.45/kWh	
Cell stack	\$134.24/kW	} (2)
BOS, ^a tanks, chemicals	99.60/kWh	
The range reflects the chromic reactant cost range from (1) \$0.32/lb to (2) \$1.30/lb.		

^aBalance of system.

TABLE 5.

Assumption or parameter	Value
FOB cost at factory, \$	4425 (1980)
Annual inflation rate, percent	8
Wholesale markup (new construction), percent	20
Retail markup (new construction), percent	33-1/3
Installation cost \$ ancillary equip., \$	1000 (1980)
Annual operating and maintenance cost	2% of installed cost
Nameplate capacity, kW/kWh	5/25
Efficiency, percent	75
Life time, yr	30

TABLE 6. - 30-YEAR LIFE CYCLE COSTS^a

	Peak/off peak ratio	Redox	Advance pb ^d	No storage grid only
New construction ^b (all electric energy efficient home)	2:1	\$142,309	\$152,123	\$131,260
	3:1	\$132,061	\$142,263	\$131,691
Retrofit (all elec- tric conventional home) ^c	2:1	\$180,470	\$179,952	\$159,202
	3:1	\$167,934	\$167,804	\$157,346

^aPresent value in 1985 \$ over a 30-year life.

^bStorage system costs included in 30-year mortgage.

^cStorage system costs financed over 5-year period.

^d5-Year battery replacement cycle at \$62/kWh.

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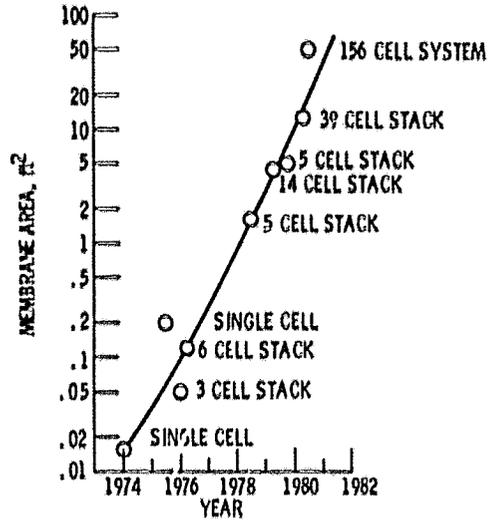


Figure 1. - Increase in membrane area of Li/PC Redox hardware.

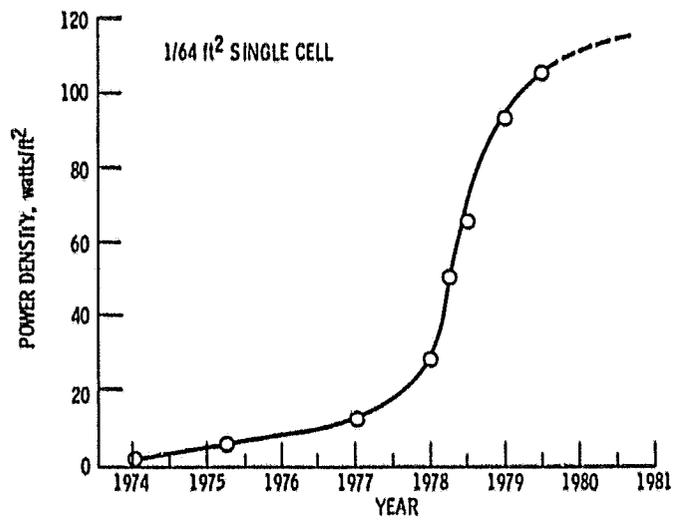


Figure 2. - Peak power performance.

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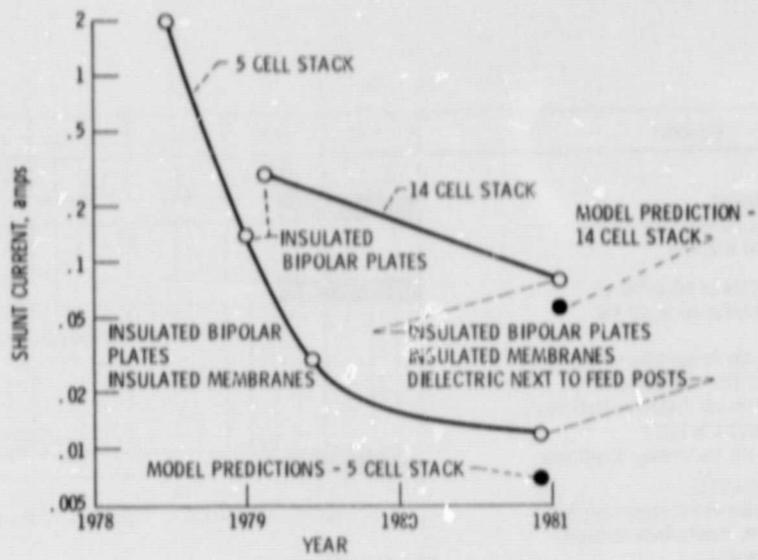


Figure 3. - Reduction in shunt currents of LeRC Redox stacks.

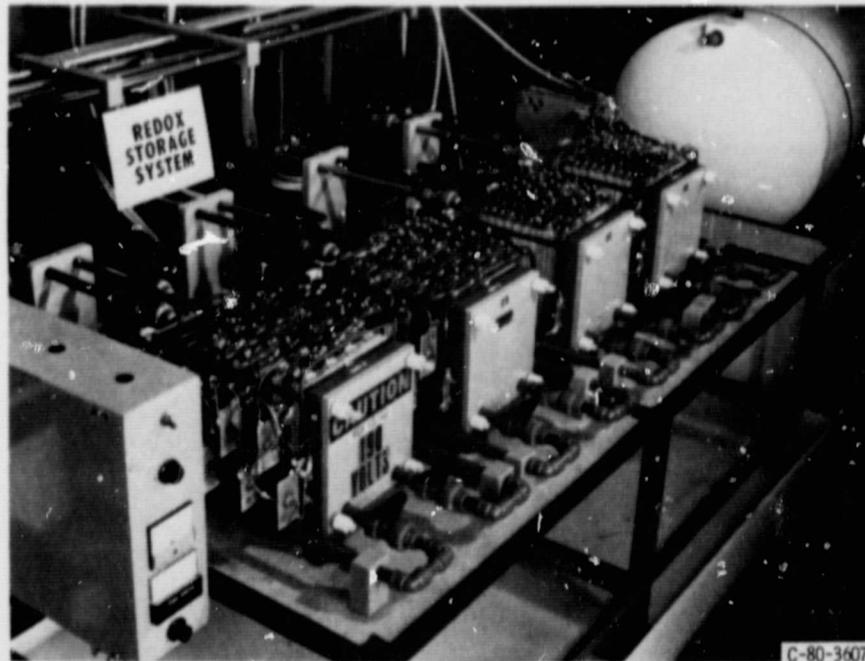


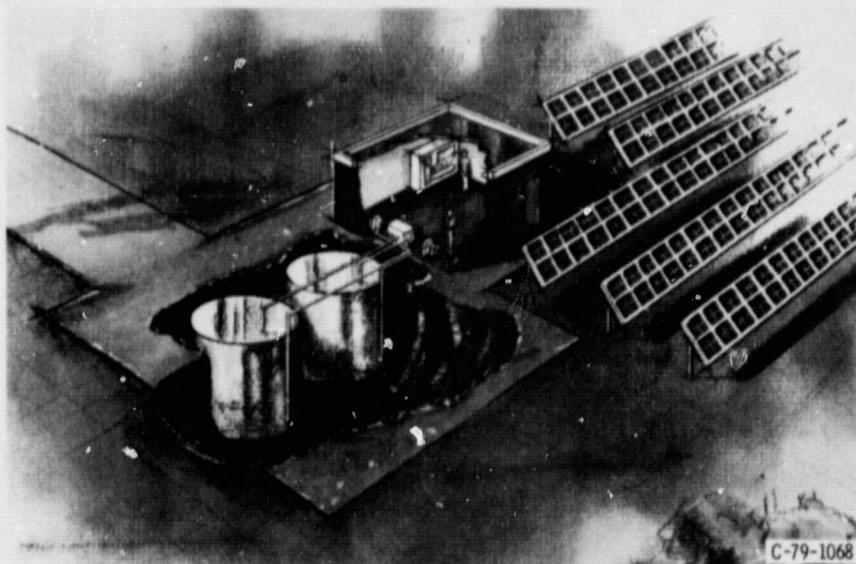
Figure 4.

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ELEMENT	CY 80		CY 81	CY 82	CY 83	CY 84	CY 85	CY 86
	A	B	A	A	A	A	A	A
1.0 PROJECT MANAGEMENT	▽	▽						
A. Annual Project Contractor's Review								
B. Redox Industrial Briefing								
2.0 PROTOTYPE SYSTEMS DEVELOPMENT								
A. Complete checkout of 1st Multi kW Preprototype								
B. Complete Multi kW Preprototype Field Test								
C. Complete Test of 100 kW Module								
D. Complete 1st Multi kW Prototype Field Test								
E. Deliver MW Modules to BEST								
F. Establish Multi kW Technology Readiness								
3.0 APPLICATIONS ANALYSIS	ELECTRODES, MEMBRANES, PJMPS, CHEMICALS, SYS. IMPROVEMENTS							
A. Prelim. institutional framework defined.								
B. Establish Prelim. Application concepts and Market Potential.								
4.0 SUPPORTING TECHNOLOGY								
DOE MANAGEMENT DECISIONS								
A. Proceed to Prototype Multi kW								
B. Proceed to Prototype Megawatt Module								
NOTES:								
LEGEND								
MILESTONE								

Figure 5. - NASA-Redox storage system development.



ARTIST'S CONCEPT OF A SMALL NASA-REDOX STORAGE SYSTEM FOR STAND ALONE APPLICATIONS

Figure 6. - Solar photovoltaic energy storage system - 10 kilowatt - 500 kilowatt hours.

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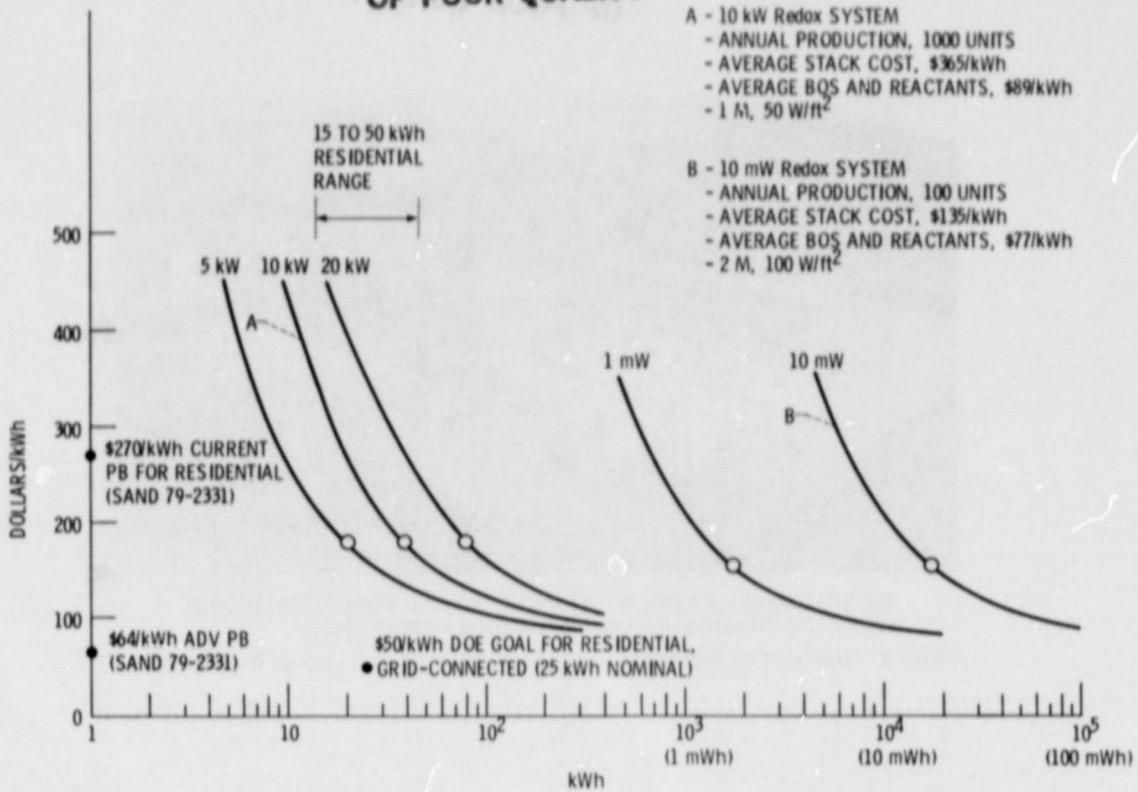


Figure 9. - Manufacturer's average selling price as a function of storage duration (data from CR165260).

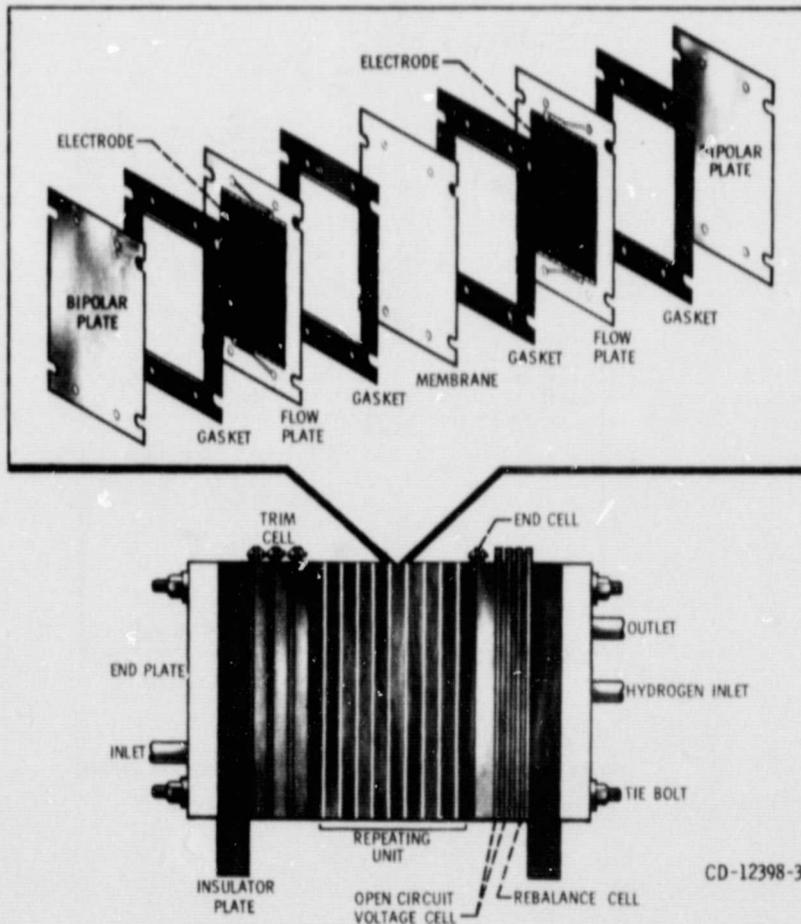


Figure 10. - Redox stack and single cell components.

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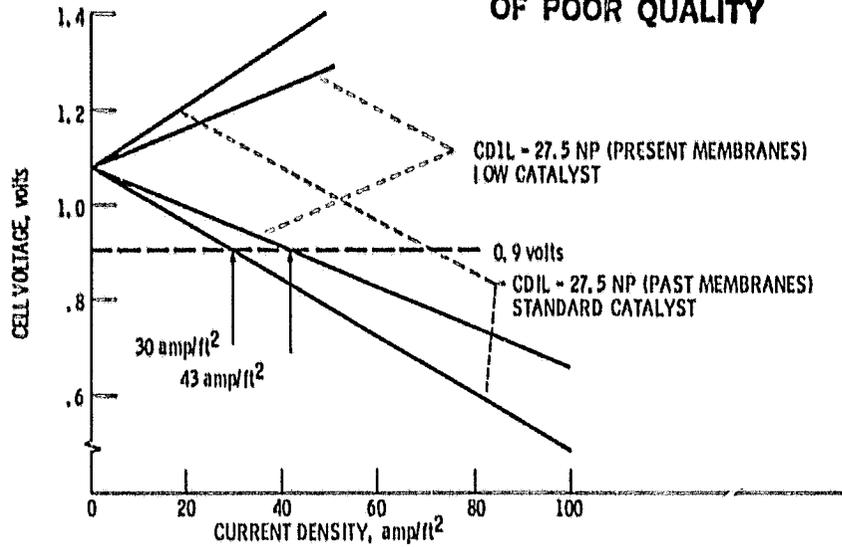


Figure 11. - Membrane performance comparisons (1 molar solutions and 50 percent DOD)

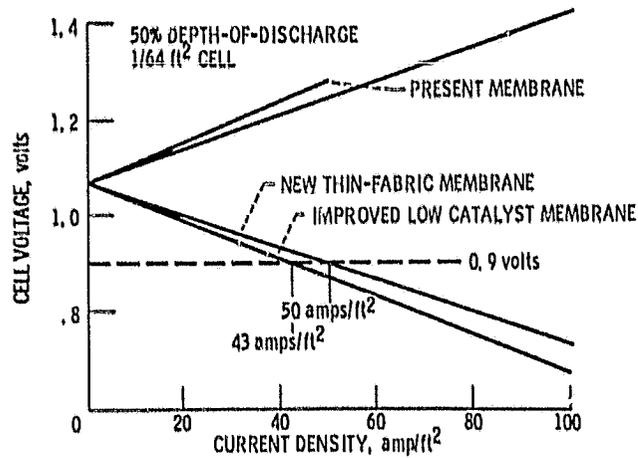


Figure 12. - Performance comparison between present and new, thin membranes (1 molar solution and 50 percent DOD).

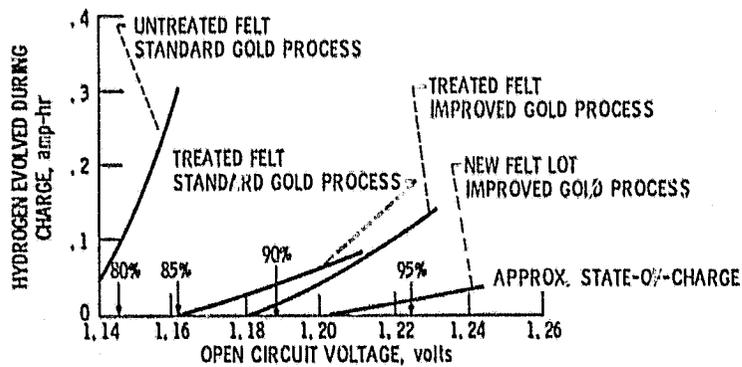


Figure 13. - Hydrogen evolution characteristics of chromium electrodes.