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REDOX FLOW CELL DEVELOPMENT AND DEMONSTRATION PROJECT

CALENDAR YEAR 1976

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

Prepared for
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16 Abstract Research and development on the redox flow cell conducted by the NASA Lewis Research Center for the Department of Energy (formerly the Energy Research and Development Administration) from January 1, 1976, to December 31, 1976, are described in this report. The major focus of the effort during 1976 was the key technology issues that directly influence the fundamental feasibility of the overall redox concept. These issues were the development of a suitable semipermeable separator membrane for the system, the screening and study of candidate redox couples to achieve optimum cell performance, and the carrying out of systems analysis and modeling to develop system performance goals and cost estimates.			
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REDOX FLOW CELL DEVELOPMENT AND DEMONSTRATION PROJECT

Calendar Year 1976

EXECUTIVE SUMMARY

The NASA Lewis Research Center is conducting research and development for the Department of Energy (formerly the Energy Research and Development Administration), Division of Energy Storage Systems, under NASA-ERDA Inter-agency Agreement E(49-28)-1002, entitled "Redox Flow Cell Development and Demonstration Project." Those efforts for the period January 1, 1976, to December 31, 1976, are described in this report. The goal of this project is to develop the redox system into a viable candidate for the bulk storage of electric energy. Because of its design flexibility, in which storage capacity and power level can be sized independently, the redox system should be especially suited for operation on a weekly energy storage cycle in a utility environment. Compared to a daily storage cycle, where conventional batteries would seem to have their greatest usefulness, a weekly storage cycle can permit 150 percent more of a utility's peak energy requirement to be supported and provides a 40 percent greater discharge power capability.

The major focus of the effort during 1976 has been to address the key technology issues that directly influence the fundamental feasibility of the overall redox concept. These issues are the development of a suitable semipermeable separator membrane for the system, the screening and study of candidate redox couples to achieve optimum cell performance, and the carrying out of systems analysis and modeling to develop system performance goals and cost estimates.

Significant improvements have been made in the semipermeable membrane in regard to the magnitude and stability of its electrical resistance and its ability to inhibit crossmixing of reactants. The following table displays the progress made in several key characteristics of membranes for the redox application. The

ultimate goals listed for these characteristics represent ideal levels, but successful system operation can be anticipated with more modest achievements.

Characteristic	1974	1976	Ultimate goal
Membrane life, hr	<24	>8000	40 000 to 80 000
Cell half-life (cross diffusion parameter), hr	150	3000	40 000 to 80 000
Membrane resistivity, Ω -cm	200	50	10
Resistance stability, hr	<1	1000	40 000 to 80 000

Most of the redox couple work to date has been performed with the aqueous iron and titanium chloride redox couples as the positive and negative electrode reactants, respectively. The iron couple has shown itself to be an excellent, well-behaved electrode material. On the other hand, the titanium couple shows a considerable loss of performance during the first several charge-discharge cycles. Chemical analysis of the reactant solutions has shown that this performance loss results from equilibration of the initial HCl supporting electrolyte concentration gradient across the membrane and, to a much smaller extent, from the oxidation of titanous ions by dissolved air. In view of this, a better negative electrode couple must be developed. A contract effort for the study of other redox couples yielded three potentially attractive choices for further study in 1977: $\text{Cr}^{+2}/\text{Cr}^{+3}$; $\text{Br}^-/\text{Br}_3^-$; and $\text{Cu}(\text{NH}_3)_2^{+1}/\text{Cu}(\text{NH}_3)_4^{+2}$.

Experimental evaluation of the effect of cell configuration, electrode type, and the reactant flow hydrodynamics on cell performance has underlined the importance of avoiding the laminar flow regime for cell reactants. Turbulence promoters and flowthrough electrodes, as well as high reactant concentrations, have been shown to greatly improve cell performance. One cell configuration, referred to as the "three stream" cell, was originally developed as a tool for

analyzing cell performance. Clearly, it also offers an alternative approach to the design of a redox system, in the event that an adequately selective membrane is not developed. In the three-stream cell the two reactant solutions are separated by two membranes between which flows a solution of the supporting electrolyte. Reactant ions diffusing into this solution would be swept from the cell and would be recovered for reuse.

Several mathematical models of the redox system have been developed for examining the effect on system cost of variations in system and cell parameters. Use of the simplest of these models suggests that the parameters having a significant effect on system cost are those that affect the energy density (Wh/liter) of the reactant solutions (e.g., concentration and reversible voltage). More complex models have also been applied, but subsequent analyses of these models reveal that excessively high system costs have been generated because of errors in component cost subroutines and other defects. System analysis work will continue to refine these models and to obtain more reliable system cost estimates.

1. PROGRAM OVERVIEW

The calendar year 1976 research and development efforts associated with the Redox Flow Cell Development and Demonstration Project are described. The project is being conducted by the NASA Lewis Research Center under Interagency Agreement E(49-28)-1002 with the Department of Energy (DOE). The project is part of the Electrochemical Energy Storage Program directed by the Division of Energy Storage Systems of DOE.

The long-term objective of this project is to develop and demonstrate a redox flow system of sufficient energy capacity to provide useful operating experience and preliminary cost data as basic input for the design and construction of large commercial systems. For the near term, attention is being focused upon the key technology issues that will determine the fundamental feasibility of the overall redox concept.

In the final analysis, storage for electric utilities will be accepted or rejected on the basis of its impact on the economics of operation of the utilities. A viable storage system will permit the utilities to increase the load factors for their more-efficient baseload generating equipment, and will reduce the demand on older,

less-efficient equipment and peaking turbines. Storage capability will also permit the utilities to increase their baseload capacities to optimum levels and to phase out, or refrain from purchasing, less-efficient equipment.

In a study performed for DOE by the Public Service Electric and Gas Company (ref. 1), load characteristics of 199 U.S. electric utility systems were analyzed. These systems represent 90 percent of the total installed capacity and 95 percent of the net energy generated in the United States. From these 199 systems, 8 were selected as being most representative of the utility industry, based on system size, peaking season, annual load factor, daily load shape, generation mix, and geographic location. For each of these 8 representative systems an optimum baseload capacity was identified which would provide the maximum amount of off-peak (storable) energy for meeting peak requirements. The analysis reveals that the theoretical maximum amount of peak energy which could be supported by off-peak storage is about 10 percent of the annual energy production. For the study year of 1971, this would amount to 160×10^9 kWh. On a practical level, assuming a weekly storage cycle and 75-percent electric-to-electric conversion efficiency and disregarding the off-peak energy which does not occur on a consistent basis during the entire year, the amount of supportable peak energy becomes 5 percent of annual energy generation, or 80×10^9 kWh nationally. Similarly, the discharge power capacity for energy storage on a typical system theoretically is 20 percent of the annual system peak power. For 75-percent conversion efficiency and a weekly cycle this discharge power capacity becomes 17 percent of the annual peak. When consideration is given to daily cycle operation under previously defined practical conditions, the amount of supportable peak energy falls from 5 percent to 2 percent of annual production, and the discharge power capacity falls from 17 percent to 12 percent of the annual peak. Because the energy storage section and the power generating section of a redox system can be independently sized, such a system is more amenable than conventional batteries, to being cost-efficiently designed for a weekly duty cycle. Thus, a redox system can be more cheaply adapted to take advantage of the higher energy and power possibilities for the weekly cycle.

Solar and wind turbine generation of electric energy, because of their intermittent output will require a storage capability. However, the economics of integrating storage devices into these systems is not as well defined as for utilities.

It may be that necessity will allow a premium to be paid for storage devices with these energy systems.

Among the various technologies contending for an electric energy storage role, one of the more attractive is electrochemical storage. Of course, no battery system of the size necessary for utility applications ever has been assembled. Present batteries, having well-developed technologies, may be troubled by cost, depth-of-discharge limitations, electrode morphology changes, and cycle-life limitations. Economic evaluation of advanced batteries is made difficult by the rudimentary state of the art.

Redox systems are not batteries in the traditional sense. Although some electrochemical technology is common to both, the redox system has a much greater similarity to fuel cell systems. The redox system being developed at Lewis is referred to as a "two tank" system because each reactant is continuously recirculated between its respective storage tank and the power-generating module. The higher-than-stoichiometric flow rates enhance mass transport at the redox cell electrodes. Also, the fact that the reactants are only fractionally depleted on each pass through the cells permits higher power densities than can be achieved with single-pass (four tank) systems. Because there is no phase change as a redox couple is charged or discharged, there are no inherent depth-of-discharge or cycle-life limitations for a redox system. Materials problems are minimized because operating temperatures are mild. An additional advantage over conventional batteries is that the energy storage capacity and the power generation capability of a redox system can be independently sized, permitting optimum reactant utilization and cost efficient design for weekly cycle operation. Also the modular character of redox system components will permit efficient expansion to meet evolving power levels and load factors.

In theory, the major drawback to a redox system is that, because of the modest energy density of its reactant solutions, it is a high-volume system. This will be reflected in costs for land and tankage. In practice, the problems encountered at Lewis revolve around the development of a suitable membrane and an adequate negative reactant/electrolyte/electrode combination for the redox system. Most of the redox project effort during 1976 has been directed toward these problems.

In the membrane area, development and evaluation were pursued in-house and under contract with Ionics, Inc. Both efforts have resulted in considerable improvements in membrane resistance stability and the ability to prevent crossmixing of reactant ions. Screening of redox couples at Giner, Inc., has resulted in the selection of three potentially attractive couples which will be evaluated in depth during 1977. Work at Giner, Inc., and in-house has given insight into the interrelationship of electrode type, cell configuration, and reactant flow hydrodynamics in regard to cell performance. Extensive study of the iron-titanium couple pair has shown the iron couple to be an admirable positive material and has resulted in an understanding of the problems associated with the negative titanium couple. A three-stream cell configuration has been developed. It is a useful analytic tool and also offers an alternative system design approach if adequately selective membranes cannot be developed. Mathematical models of the redox system are being developed to determine the effect on system cost of variations in cell operating parameters.

It is anticipated that the continuation of these efforts during 1977 will go a long way toward showing that the redox storage system concept is an attractive technology for electric utilities.

II. MEMBRANE DEVELOPMENT

Investigation early in the Redox Flow Cell Development and Demonstration Project revealed that no commercially available anion-exchange membranes could meet the requirements of the Lewis redox cell. These requirements include low resistivity, high ion-exchange capacity for the restriction of metal-ion transport, stability in the redox cell environment, and ease of manufacture and handling. Parallel efforts are being carried out in-house and under contract to develop new membranes or to modify existing ones to meet these requirements. The membranes being studied under contract are homogeneous films of copolymerized or crosslinked ion-exchange monomers on a fabric support. The in-house membranes are heterogeneous mixtures of Kraton [®] rubber, materials with amine functional groups, and, in some cases, inert fillers. These mixtures are coated onto an asbestos substrate or extruded as films.

Contract Membrane Development

The current membrane development program at Ionics, Inc., began in July 1976 and is a follow-on to the contract effort by that company in 1974-75. Three major tasks are included in this program:

(1) Synthesize and screen new or unproven membranes (eight in all) for the redox cell application. Screening parameters are ion-exchange capacity, water content, resistance, and ferric ion permeation rates.

(2) Optimize the six most promising candidate membranes (three identified in the initial program and three from the preceding task). Optimization is directed toward increasing selectivity for cation transfer, minimizing resistivity, and enhancing durability in the redox cell environment. Variations in solvent content, water content, crosslink type, and crosslink density are being evaluated.

(3) Scale-up membrane fabrication for the optimized systems to demonstrate production capabilities, and a detailed characterization of electrical and physical properties.

During 1976, three of the eight Task 1 materials were prepared and tested. Preliminary results were as follows:

(1) System CDIL (vinylbenzylchloride crosslinked with dimethylaminoethylmethacrylate on a cloth support): This is a "self-crosslinking" resin which shows good durability and very good selectivity for exclusion of Fe^{+n} . Initial problems with pin-hole formation during preparation appear to have been overcome, and this system is a prime prospect for continued study. It exhibits exceptional selectivity, conductivity, and durability in the redox environment.

(2) System VC (commercial vinylchloride film aminated with tetraethylene-pentamine): The tough, flexible nature of these unsupported membranes is most desirable. However, to date they have not consistently shown adequate selectivity and conductivity.

(3) System CE (vinylbenzylchloride crosslinked with ethylenediamine on a cloth support): This "self-crosslinking" system offers excellent potential for high ion-exchange capacity (desirable for both good ion exclusion and con-

ductivity). However, to date, useful membrane samples have not been reproducibly obtained.

The three most promising membranes from the first contract program were studied to determine compositions and procedures for fabrication of membranes having optimal selectivity and conductivity in the redox environment. The current status of these systems is

(1) System 103Q2L (vinylbenzylchloride crosslinked with divinylbenzene and aminated with trimethylamine on a cloth support): This is an improved version of a commercially available membrane which has performed quite well in the redox environment. Recent formulations of this membrane system have shown significant reductions in the transport of cations in the test environment.

(2) System B2L (vinylbenzylchloride crosslinked with divinylbenzene and aminated with diethylenetriamine on a cloth support): The ethyleneglycoldimethacrylate crosslinks of the original formulation were replaced to improve erosion resistance of the resin. However, the current formulation does not show adequate durability in the redox environment and appears to lose both selectivity and conductivity during use.

(3) System A3L (2-vinylpyridine crosslinked with divinylbenzene on a cloth support): This system exhibits good electrical and physical properties and appears very desirable for acidic solutions. Cracks sometimes appear in large samples, however; and variations in its preparation have been considered to circumvent this problem.

Data for the latter three systems, plus the CDIL membrane, are shown in table 1. The effect of membrane water content on ferric ion selectivity is significant.

In-house Membrane Development

The prototype heterogeneous membrane formulation developed at Lewis consists of Kraton[®] rubber, crosslinked vinylpyridine, and magnesium zirconium silicate filler. This formulation, designated as DS-156, is generally coated onto an asbestos substrate but also has been extruded as a film. Variations of this formulation, plus samples of the homogeneous membranes developed at Ionics, Inc., have been evaluated in operating redox cells. The configuration

TABLE 1. - PHYSICAL PROPERTIES OF SELECTED
IONICS, INC., MEMBRANES

Membrane	Ion exchange capacity, milliequivalents per dry gram	Water content, percent	Resistance, $\Omega\text{-cm}^2$		Iron ion transport rate, $P_{\text{Fe}^{+2}}$, mg Fe/m ² /hr
			$a_{R\zeta}^C$	$b_{R\zeta}^J$	
103QZL:					
New	2.24	25.4	10.6	7.2	2 to 3
Old	2.34	36.6	9.5	4.1	1000 to 3200
B2L:					
New	3.53	27.7	8.7	10.1	1 to 2
Old	5.38	41.9	8.0	----	30
A3L					
New	3.10	31.6	9.1	9.6	1 to 2
Old	3.12	39.8	9.4	----	70
CDIL					
New	3.91	31.3	6.9	----	2
Old	4.05	41.8	4.9	----	50

^aMeasured by contact probes in 0.1 N HCl at 25° C.

^bMeasured by liquid junction method in 1.0 N HCl at 25° C.

Figure 1. - Configuration of laboratory redox cell.

of these cells, shown in figure 1, consists of graphite cloth electrodes sandwiched between the test membrane and the respective graphite foil current collectors. The active cell area is 14.5 cm^2 . In most cases the redox solutions used have been 1 M FeCl_3 (0.5 N HCl) and 1 M TiCl_3 (6.0 N HCl). Testing has consisted of repetitive charge-discharge cycles.

The primary criteria for evaluating the membranes have been resistance, resistance stability, and the "iron transport half-life" of the cell. This latter term is defined as the extrapolated time required for one-half of the iron ions originally present to cross the membrane into the titanium half-cell. This "time" is fictitious, in that infinite time would be required for the iron concentration to become equal on both sides of a membrane. It serves well, however, as a screening parameter. Cell resistance was periodically measured with an alternating-current bridge at 1000 Hz. Spectrophotometric analysis of periodically taken samples of the respective reactant solutions established the cell half-life. In addition, chemical analyses were made to determine transference numbers, charging efficiencies, and the nature of possible side reactions. The concentrations of reduced metal ions in the sample were measured by potentiometric titration with KMnO_4 , using a platinum indicator electrode and a silver-silver chloride reference electrode. The cutoff potentials are +300 mV for Ti^{+3} and +700 mV for Fe^{+2} . The oxidized species concentrations were then determined by difference after completely reducing the sample in a Jones reductor and repeating the titration. Chloride ion concentration was measured by a potentiometric titration with AgNO_3 , and hydrogen ion concentration was calculated from charge-balance considerations.

Some general conclusions can be drawn from the chemical analyses performed (ref. 2):

- (1) A greater portion of cell current is carried by protons than by chloride ions, even though the membranes are designed to be anion exchangers.
- (2) Titanium diffusion rates through the membranes are roughly equivalent to those of iron.
- (3) Equilibration of acid concentrations occurs quite rapidly when the half-cell acidities initially differ.

The results from the evaluation of six membranes produced during the initial contract with Ionics, Inc., are presented in table 2. The projected half-lives range from about 400 hours to about 2000 hours. The resistances are quite stable for as long as 1 month of testing. Judging from the reduction in iron permeability achieved by Ionics, Inc., for improved versions of three of these membranes (table 1), it is expected that in-house evaluation of these three will show much greater projected half-lives than those given in table 2.

A handmade baseline in-house membrane (DS-156) was compared with a membrane of the same formulation produced on a continuous slurry-coating machine (DS-156D). The machine-coated material apparently has a much tighter structure because its iron-transport half-life was 2900 hours as compared with 600 hours for the handmade sample. Also, the resistance for DS-156D was 1.0 ohm, as compared with 0.6 ohm for DS-156.

Other handmade membranes consisting of an asbestos substrate coated on one side with a tertiary amine-bearing material (vinylpyridine) and on the other side with a quaternary amine-bearing material (IRA-400) have been tested. The data in table 3 show a significant improvement in iron transport half-life when the tertiary amine faces the iron solution. The first two membranes in the table differ only in their orientation in the test cell. The first pair of membranes differs from the second pair in that the latter contains magnesium zirconium silicate filler. The K9098R membrane is especially attractive because of its low and stable resistance. It is expected that machine production of these membranes would result in even greater half-lives. Work is continuing in this area.

The baseline heterogeneous formulation was successfully extruded as a film (as opposed to being coated on an asbestos substrate). However, initial runs produced overly porous membranes. Reduction of the ionic-material content of the formulation should alleviate this problem.

III. CELL COMPONENT SCREENING

In parallel with the development of membranes suitable for the redox cell, it is necessary to evaluate the effect that other factors have on cell performance. These include the redox couple pair, the supporting electrolyte, the electrode

TABLE 2. - IRON TRANSPORT HALF-LIFE AND RESISTANCE
FOR IONICS, INC., MEMBRANES

Membrane	Projected iron half-life, hr	Resis- tiv- ity, Ω -cm	Initial resistance, Ω	Resistance change, Ω /day
ASL-28A	780	134	0.47	0.0055
ASL-28A ^a	795	---	----	-----
B2L-DT34A	1030	171	.60	.0005
A4L-28A	2050	126	.44	.0025
A4L-28A ^a	1550	126	.44	.0025
VCI-TP-12X	370	91	.32	-.0008
VCI-TP-12X ^a	470	117	.41	-.0058
B2L-DT95	1365	171	.60	-.0029
QZL-219	985	143	.50	.0061
QZL-219 ^a	1170	160	.56	.0107

^aDuplicate test.

TABLE 3. - EFFECT OF ION EXCHANGE GROUP ON HALF-LIFE AND RESISTANCE

Membrane	Orientation: tertiary amine facing titanium or iron solution	Projected iron half-life, hr	Resistivity, Ω -cm	Initial resistance, Ω	Resistance change, Ω /day
K7174R	Ti	2100	323	1.13	0.044
K7471R	Fe	5600	328	1.15	.018
K9890R	Ti	3500	422	1.48	.028
K9098R	Fe	4700	231	.81	-.005

materials, and the overall cell configuration. Most of the in-house effort during 1976 focused on the iron-titanium couple pair, and most of the testing was performed on the standard laboratory cells described in section II and figure 1.

Redox Couples

Among the characteristics desirable in a redox couple are a relatively high reversible potential; fast kinetics during charge and discharge; reversibility; high solubility; simple, one-step charge transfer reactions; and an absence of side-reactions with the electrodes or electrolyte. Of course, some of these characteristics (e.g., reaction kinetics) are strongly influenced by the electrode being used.

Giner, Inc., was awarded a contract to examine potentially attractive couples with regard to some of these factors. This contract was carried out in two phases: a broad investigation of the basic characteristics and behavior of various redox couples, followed by a more limited investigation of their electrochemical performance in a redox flow reactor configuration.

The primary objective of the first phase of the program was to evaluate eight redox couples under a variety of conditions in terms of their exchange current densities as measured by the rotating-disk electrode procedure. The redox couples investigated in this first phase were $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{Ti}^{+3}/\text{Ti}^{+4}$, $\text{Cr}^{+2}/\text{Cr}^{+3}$, $\text{Sn}^{+2}/\text{Sn}^{+4}$, $\text{Br}^{-}/\text{Br}_3^{-}$, $\text{Sb}^{+3}/\text{Sb}^{+5}$, $\text{Cu}(\text{NH}_3)_2^{+1}/\text{Cu}(\text{NH}_3)_4^{+2}$, and $\text{Cr}(\text{CN})_6^{-4}/\text{Cr}(\text{CN})_6^{-3}$. Ideally, the couples were to be tested on gold and graphite electrodes at 80 and 120 F; reduced-to-oxidized ratios of 1:10, 1:1, and 10:1; and total concentrations of 1 M, 3 M, and 6 M. In actual testing, solubility and corrosion effects frequently limited the range of conditions.

The results* from the first phase (table 4) showed the more-promising couples to be $\text{Fe}^{+2}/\text{Fe}^{+3}$, $\text{Br}^{-}/\text{Br}_3^{-}$, $\text{Ti}^{+3}/\text{Ti}^{+4}$, $\text{Cr}^{+2}/\text{Cr}^{+3}$, and $\text{Cu}(\text{NH}_3)_2^{+1}/\text{Cu}(\text{NH}_3)_4^{+2}$. The $\text{Fe}^{+2}/\text{Fe}^{+3}$ and $\text{Br}^{-}/\text{Br}_3^{-}$ couples were chosen as the positive electrodes in the second phase of testing for their high exchange current

*The contractor's final report (ref. 3) contains more-detailed information and should be consulted for an in-depth review and understanding of this topic.

TABLE 4. - APPROXIMATE EFFECTIVE EXCHANGE CURRENT AND
REVERSIBLE POTENTIAL

Couple	Exchange current density, i_0 , mA/cm ²	Reversible potential, E^0 , V (as compared with saturated calomel electrode)
Anodes		
$\text{Cu}(\text{NH}_3)_2^{+1} / \text{Cu}(\text{NH}_3)_4^{+2}$	20	-0.3
$\text{Ti}^{+3} / \text{TiO}^{+2}$ (6 M HCl)	1	-.1
$\text{Cr}^{+2} / \text{Cr}^{+3}$ (1 M HCl)	0.1 to 1	-.4
$\text{Sn}^{+2} / \text{Sn}^{+4}$ (3.5 M HCl)	0.01 to 3	-.1
Cathodes		
$\text{Br}^- / \text{Br}_3^-$ (NaBr)	3	+0.8
$\text{Fe}^{+2} / \text{Fe}^{+3}$ (1 M HCl)	10	+.5
$\text{Sb}^{+3} / \text{Sb}^{+5}$ (3 M HCl)	.1	+.6

densities and reasonable solubility limits; $\text{Br}^-/\text{Br}_3^-$ also has a very high open-circuit for operation as a positive electrode. The $\text{Cr}^{+2}/\text{Cr}^{+3}$ and $\text{Cu}(\text{NH}_3)_2^{+1}/\text{Cu}(\text{NH}_3)_4^{+2}$ couples were chosen for study, as negative electrodes, due to their reasonably high exchange current densities. (The titanium couple, although better than the chromium couple, was not chosen in order to avoid duplication of previous extensive study at Lewis.)

The second phase of the program involved the testing of these four couples in a redox reactor under flow conditions with a variety of electrode materials and structures. The best performance with the negative electrode couples was obtained with the $\text{Cu}(\text{NH}_3)_2^{+1}/\text{Cu}(\text{NH}_3)_4^{+2}$ couple, particularly when a gold screen electrode was used in a frontal structure (i.e., electrode placed against the ion exchange membrane with electrolyte flowing on the back). The best performance with the positive electrode couples was obtained with the $\text{Br}^-/\text{Br}_3^-$ couple, particularly with a porous carbon electrode in a recessed structure (described in REDOX CELL CONFIGURATIONS section). The $\text{Fe}^{+2}/\text{Fe}^{+3}$ couple using a graphite woven-cloth electrode (as has been studied at Lewis) also showed very good performance. The considerable effect of electrode material, structure, and cell configuration on cell performance suggests that much attention must be given to the optimization of a cell for a given redox couple.

The kinetic behavior of the iron couple was also studied at Lewis with the rotating-disk electrode (RDE) technique (ref. 4). Edge-on pyrolytic graphite (EOPG) electrodes were used in HCl-acidified solutions with total iron concentrations ranging from 0.2 to 3.3 M. The range of oxidized-to-reduced species concentrations was from 1:10 to 10:1.

In figure 2, polarization curves are shown for three RDE rotational speeds in the 1 M $\text{FeCl}_2/2$ M $\text{FeCl}_3/0.5$ N HCl system. Also shown is the Tafel plot derived by extrapolating these data to infinite rotational speed. This particular set of data reveals two distinct Tafel slopes when the electrode is polarized anodically. Extrapolation of the Tafel plots to the points of zero polarization gives exchange currents of 13.5 and 29.4 mA/cm^2 , indicating good electrode kinetics for the iron couple. The exchange current density, when expressed as a standard rate constant ($k_s = i_0 / [\text{Fe}^{+3}]^{1/2} [\text{Fe}^{+2}]^{1/2} \mathcal{F}$), is quite insensitive to total iron ion concentration over the range of concentrations studied. This is encouraging because total system cost can be significantly reduced by increasing reactant concentration.

Figure 2. - Polarization curves and Tafel plot for edge-on pyrolytic graphite (EOPG) rotating disk electrode (RDE) in the 1 M FeCl_2 /2 M FeCl_3 /0.5 N HCl system (i.e., exchange current density, mA/cm²; b , Tafel slope, volts per decade; area of disk, 0.32 cm²).

Several of the redox couples examined by Giner, Inc., were paired and evaluated in laboratory cells at Lewis. Discharge curves for these couple pairs are presented in figure 3. The poor coulombic efficiency for the cells with a chromium anode is typical for graphite cloth electrodes and probably results from a combination of hydrogen evolution during charge, reduction of the solvent by the chromous ion, and air-oxidation of the chromous ion. Because of the attractive open-circuit potential for the iron-chromium pair, it will be subjected to intensive investigation during 1977. (All cells except the iron-titanium cell were very difficult to charge.)

Electrode Materials

The desirable characteristics for a redox cell electrode include high conductivity, high surface area, high gas evolution overpotential, catalytic activity during charge and discharge, and chemical stability toward the reactant solution. Because most of the in-house effort this year has focused on the iron-titanium pair, for which graphite cloth and felt are excellent electrode materials, not much screening of other electrodes has been done. However, lead plates and sinters were examined as a possibility for the chromium couple, because this metal has a high hydrogen evolution overpotential. The lead electrode for a short while permitted chromium charging rates about twice as high as did graphite. Reaction of the lead with the acid electrolyte then slowly resulted in passivation. There was no improvement over graphite in charging efficiency.

During the cell component screening program at Giner, Inc., electrode materials examined for the various redox couples included various forms of platinum, gold, titanium, carbon, graphite, and ruthenium oxide. Although results were greatly influenced by cell configuration, flow rates, and other operational factors, they show that graphite cloth, porous carbon, and gold were the best materials for the iron, bromine-bromide, and copper-ammonium complex couples, respectively. None of these materials proved to be of value for the chromium couple.

Figure 3. - Open-circuit potential versus discharge time for selected redox couple pairs.

Redox Cell Configurations.

In the work at Giner, Inc., it was shown that the performance of a given electrode/redox couple combination could be greatly influenced by the overall cell configuration. During the course of this study, three broad types of cell structures were considered:

(1) Frontal electrode structures: The electrode was a porous open structure like screen or graphite paper. It was placed in contact with the ion exchange membrane, and the reactant-electrolyte flowed behind the electrode through a "pin" field in the back plate of the cell.

(2) Recessed electrode structures: The electrode was either a nonporous sheet like platinized titanium sheet or a microporous structure like carbon or activated carbon. It was located against the back plate of the cell with coarse plastic screen between the electrode and the ion exchange membrane, permitting reactant-electrolyte to flow in front of the electrode.

(3) Cavity filling electrode structures: A typical example of this structure used the graphite woven-cloth electrode as in the Lewis experiments. This type of electrode filled the cavity, and the reactant-electrolyte flowed through the structure.

Structure 2 proved to be the best for the bromine-bromide and copper-ammonium complex couples; structure 3 was most suitable for the iron couple.

During the experimental work at Lewis, the question arose whether the crossmixing of reactants through the membranes, in addition to affecting the coulombic capacity of the cell, had some additional effect on the cell performance. This led to the development of the three-stream cell (fig. 4), in which two membranes are used to more effectively isolate each half-cell from the reactants of the other. Performance of the three-stream cell and the standard cell configuration, under identical conditions and with the iron-titanium pair, is compared in figure 5. In this comparison it was noted that the reactant crossmixing rate was decreased by a factor of 10 for the three-stream cell. The greatly superior performance of the three-stream cell was unexpected, in that it has two membranes interposed between the electrodes, instead of one. There is evidence, discussed in the next section, that the poorer per-

Figure 4. - The three-stream cell.

Figure 5. - Performance comparison of three-stream and standard redox cell configurations.

formance of the standard cell is not due to the crossmixing of reactants, per se, but to the interaction of the two reactants within the single membrane.

In the case that a less-than-perfect membrane is developed for redox application, the three-stream configuration presents a very attractive fall-back position. From a system standpoint, the reactants that escape the respective half-cells are swept away by the acid solution flowing slowly between the membranes. These reactants could possibly be separated in an ion-exchange column and returned to their respective storage tanks.

To simplify cell fabrication and to reduce cell thickness and internal resistance, some development work was done on "composite membranes." In these, large-surface-area catalytic electrode material is bonded directly to the surfaces of an ion exchange membrane (fig. 6). Materials examined were carbon powder and paper; graphite powder, fiber, and felt; and palladium powder. These materials were bonded to ion-exchange membranes or microporous membranes by solvent-slurry coating or hot pressing. In cells with the iron-titanium pair, the voltage-current performance of hot-pressed graphite fiber or felt on microporous polyvinylchloride films was equivalent to that of the standard test cell. A similar composite membrane using palladium powder initially gave twice the performance of the standard cell, but the metal slowly dissolved in the acidic electrolyte.

Although these composite membranes offer some interesting possibilities, they proved difficult to fabricate. At present, no further work is being done in this area.

Electrolyte (Reactant) Solutions

When evaluation of the iron-titanium couple pair first began at Lewis, it was decided to use 0.5 N HCl as the supporting electrolyte for the iron couple, and 6 N HCl for the titanium couple. It was felt that this was necessary to minimize the formation of anionic iron chloride complexes which might pass with ease through the anion-exchange membrane and to prevent the precipitation of titanium dioxide. At that time the chemical analyses discussed in section II were not yet in use, so it was not realized that equilibration would

Figure 6. - Redox cell with composite membrane.

Figure 7. - Effect of HCl concentration on initial iron-titanium cell open-circuit voltage.

quickly bring these two acid concentrations to about 3 N. Therefore, tests were made to determine whether this choice of acid concentrations was detrimental to cell performance. Figure 7 shows that increasing the acid concentration in either reactant causes a decrease in cell open-circuit voltage. However, figures 8 and 9, showing the effect of acid concentration on load voltage, reveal that, in fact, the choice of 6 N HCl for the titanium electrolyte and 0.5 N HCl for the iron electrolyte was a good one. These last two figures also show that once the electrolytes equilibrate to about 3 N HCl, cell performance has become quite poor. To determine how rapidly this equilibrium occurred, a cell with the 0.5 N-to-6 N acid gradient was compared with one in which both electrolytes had 6 N acid. Figure 10 shows that the cell with the acid gradient suffered considerable performance loss during early cycles, while the performance of the cell with no gradient was quite stable.

These results explained, in part, an often-noticed problem with the iron-titanium couple pair: a rapid cycle-to-cycle loss in cell performance during the early stages of cell testing. To determine whether any other phenomena were occurring in addition to the equilibration of acid concentrations, two "common ion" cells were evaluated. In these, the oxidized form of a redox couple (e.g., Fe^{+3}) was the cathodic reactant and the reduced form (e.g., Fe^{+2}) was the anodic reactant. In each cell the acid concentration was the same on both sides of the membrane in order to eliminate equilibration as a factor in cell performance. Figure 11 shows that the first five discharges for the iron common-ion cell were virtually identical. However, as shown in figure 12, there was a loss of about 110 mV during the first four discharges of the titanium cell. The causes of this behavior are not yet completely understood, but oxidation of the titanous ion by dissolved air is a probable contributor. Anyway, the titanium half-cell now has been positively identified as the source of the time-dependent loss of performance in cells with the iron-titanium couple pair.

It is quite likely that no membrane will be developed that has perfect selectivity (i.e., that completely eliminates crossmixing of reactant ions). To determine the ultimate effect of such crossmixing, a cell was run in which the iron and titanium solutions were premixed. The performance of this cell

Figure 8. - Effect on cell performance of HCl concentration in the iron electrolyte.

Figure 9. - Effect on cell performance of HCl concentration in the titanium electrolyte.

Figure 10. - The effect of acid gradient equilibration on cell performance.

Figure 11. - Cycle reproducibility for the iron common-ion cell.

Figure 12. - Cycle reproducibility for the titanium "common-ion" cell.

is compared with that of a cell with fresh, unmixed reactants in figure 13. Although complete solution mixing resulted in a loss of about 40 mV in open-circuit voltage at various levels of discharge, the loss in load voltage was less than 10 mV. The implication of this result is that the degree of crossmixing, per se, has very little effect on cell performance. However, the performance comparison of a standard cell having fresh, unmixed reactants and a three-stream cell (fig. 5) showed a 100-mV advantage for the three-stream cell (i.e., the cell in which neither membrane nor electrode is exposed to both reactants). It seems, then, that there are two major problems with a cell of standard configuration when the iron-titanium couple pair is used:

(1) There is an immediate performance penalty, which results either from the exposure of the membrane to both concentrated reactants and/or from the exposure of one (or both) of the electrodes to minute amounts of the crossing-over reactant.

(2) There is an additional, as-yet unexplained, loss of performance for the titanium half-cell during early cycles. There was also an early operational problem with the iron-titanium couple pair, due to the ease of chemical oxidation of the Ti^{+3} ion. The diffusion of air into the cell test system was causing a "chemical discharging" of the titanium couple. The cell would then accept only enough electrical charge to recharge the iron couple, leaving the titanium couple in a partially discharged state and indicating a loss of capacity. For testing purposes, this problem was alleviated by using a nitrogen blanket for the test system and by using an excess of charged titanium solution. In this way it was possible to operate for extended periods of time, always having sufficient Ti^{+3} available to match the capacity of the iron half-cell.

IV. SMALL-SCALE SYSTEM EXPERIMENTS

Multicell Stacks

An analytical study at Lewis (ref. 5) has shown that when redox cells are connected hydraulically in parallel between common electrolyte manifolds,

Figure 13. - Performance comparison of mixed reactants with unmixed reactants.

parasitic circulating currents will develop. If inadequate attention is given to the design of the manifolds and cell reactant ports, these circulating currents can represent a significant loss in power and capacity.

A six-cell stack (fig. 14) with high-resistance (large L/D) reactant ports was designed, assembled, and evaluated for circulating current losses. The evaluation consisted of measuring the stack voltage first with the cell reactant cavities and manifolds flooded and then with the cavities flooded but with the manifolds drained. When the manifolds were flooded, which allowed the circulating currents to exist, the stack voltage was about 0.5 percent less than when the manifolds were drained. This result compared well with the prediction of the model and gives encouragement that the circulating current problem can be minimized. However, there will be a trade-off against the greater pump power necessitated by the high-resistance cell reactant ports.

Redox Storage for Solar Photovoltaic Array

At the request of the Photovoltaic Technology Branch at Lewis, a laboratory-scale redox system (fig. 15) was designed to provide energy storage for a solar cell array. The design concept was to use two separate redox cells sharing common reactant solutions. One redox cell was to deliver power continuously to a fixed-resistor load, while the other was to recharge the reactant solutions. A simple relay was used to isolate the charging redox cell from the solar cell array when the array output voltage fell below a preset value. This prevented the charging redox cell from discharging through the array. The test stand (fig. 16) was designed to continuously monitor the solar cell array electrical output and the current, voltage, and integrated ampere-hours for the two redox cells. The combined systems operated continuously for 2 months (ref. 6) and presented neither operational nor interface problems. These encouraging results suggest that a redox system can be a technically viable storage candidate for solar photovoltaic power generation.

C-75-4199

Figure 14. - Stack of six redox cells, hydraulically in parallel.

CS-78959

Figure 15. - Redox energy storage system for solar photovoltaic power source.

Figure 16, - Test stand for combined redox and solar photovoltaic systems.

V. SYSTEM STUDIES

The primary purpose of this effort was to develop a series of computer models of the redox system. Each model represents an increase in the level of sophistication over the preceding versions. These models are being used to identify the parameters to which system cost is most sensitive. This information will permit the establishment of cell performance goals and cell component characteristic goals for the redox cell development effort. Also, an extensive bibliography has been developed of literature on electric utility operation, electrochemical technology, and the various methods proposed for electrical energy storage. In addition, a tabulation has been prepared of the requirements which must be met by a storage system in order to be attractive to the electric utilities. Finally, an inclusive collection of comparative data for electrochemical devices proposed for utility storage applications has been compiled and analyzed. The major portion of this work was performed under contract by the Government Research Laboratories of the Exxon Research and Engineering Co., with consultation by the Public Service Electric and Gas Co. (PSE&G).

The first redox system model in this effort was developed at Lewis (ref. 7) and is referred to as the Stage Zero model. In a slightly modified form this model was programmed for the computer and was used in a preliminary parameter sensitivity analysis. The results of this analysis (fig. 17) show a large effect on system cost for variations in cell operating voltage, system voltage, and cell current density.

The next system model (Stage 1) was developed in outline form at Lewis and represented the starting point for the contract effort with Exxon Corp. The Stage 1 model assumed time-averaged values for all system parameters such as voltage, power level, and electrolyte concentrations. In its initial form the model was limited to the simulation of daily cycles only. Subsequent modifications enabled the model to accommodate weekly cycles consisting of fixed daily charge/discharge power levels and variable daily charge/discharge times. Optimization routines are used to find the charging current density that results in minimum system cost. These additional capabilities of the

Figure 17. - Redox system parameter sensitivity. Stage zero model.

TABLE 5. - RATING CRITERIA FOR ESTABLISHING FIGURE OF MERIT
FOR SELECTED BATTERY SYSTEMS

Parameter	Value of 1 Assigned if:	Value of 2 Assigned if:
Average operating voltage, V	≤ 1.00	≥ 1.00
Maximum ampere-hour capacity reported, Ah	≤ 100	≥ 100
Operating temperature, °C (°F)	≥ 100 (212)	≤ 100 (212)
Cycle life, number of cycles	≤ 1000	≥ 1000
Depth of discharge, percent	≤ 50	≥ 50
Watt-hour efficiency, percent	≤ 75	≥ 75
Energy density, Wh/kg (Wh/lb)	≤ 55 (≤ 25)	≥ 55 (≥ 25)
Power density, W/kg (W/lb)	≤ 55 (≤ 25)	≥ 55 (≥ 25)
Cost, \$/kWh	≥ 50	≤ 50

modified version of the Stage 1 model should make it a useful tool for examining the operational flexibility and design possibilities of the redox concept.

The original and modified versions of the Stage 1 model have been used by the contractor and at Lewis to examine the sensitivity of system cost to changes in system design parameters. The conclusions reached as a result of these studies have been reported in the contractor reports and in the monthly Management Information and Control System (MICS) reports prepared at Lewis for NASA and DOE Headquarters. However, it recently has been determined that some of the subroutines for calculating the costs of certain system components are in error and have been generating excessively high numbers. As a result, many of the conclusions reached and reported concerning the cost of redox systems and the effect of certain operational parameters on these costs are badly distorted. The models will be corrected and the studies repeated.

The Stage 2 model, which still is being developed, will be able to handle any charge/discharge power profile. It will take into account the effect of time-dependent reactant concentrations on electrochemical parameters (polarizations, current density, etc.) and the effect of hydrodynamic conditions on cell mass transport.

Performing a comparative analysis of available data for the possible electrochemical devices for energy storage was made difficult by the differing levels of the state of the art for the respective systems. However, by applying the criteria in table 5 to the collected data, the following systems were determined to be attractive candidates:

- Lead-acid
- Zinc-halogen
- Metal-air
- Alkali metal sulfides
- Redox

The requirements which must be met in order for a storage system to be attractive to the electric utilities are presented in tables 8 to 10. These data represent values or ranges of values derived from the study of a broad spectrum of electric utilities throughout the Nation. Included in the tables

TABLE 6. - RANGES OF STORAGE SYSTEM DUTY CYCLE OPERATING PARAMETERS
SUPPORTABLE ON U.S. ELECTRIC UTILITY SYSTEMS

Duty-cycle characteristics	Type of operation			
	Intermediate duty		Peaking duty	
	Daily cycle	Weekly cycle	Daily cycle	Weekly cycle
Discharge time, h/day	9 to 14	9 to 14	1 to 9	1 to 9
Charge time, h/day:				
Weekday	5 to 9	5 to 9	5 to 9	5 to 9
Weekend	-----	14 to 34	-----	14 to 34
Ratio of charge power to discharge power ^a	1.3 to 3.7	0.8 to 2.4	0.15 to 2.4	0.1 to 1.5
Storage capability, h	9 to 14	17 to 47	1 to 9	2 to 30
Annual operation (annual discharge time), h	2300 to 3600	2300 to 3600	250 to 1000	250 to 1000

^aFor storage systems with turnaround efficiency of 75 percent.

TABLE 7. - TIE-IN VOLTAGE AND POWER LEVEL FOR UTILITY
ENERGY STORAGE APPLICATIONS

Storage system locations ^a	Connection (tie-in) voltage, KV	Discharge power level, MW
Substation	4 to 34.5	^b 10 to 100
Switching station	26 to 230	^b 10 to 200
Central station	138 to 500	^c 500 to 2000

^aIntermediate and peaking duty and daily and weekly cycle storage systems all appear to be useful at each location.

^bThe larger power levels would probably apply to weekly storage cycles.

^cThe larger power levels represent the maximum power associated with current pumped-water storage technology.

TABLE 8. - ELECTRICAL INTERFACE REQUIREMENTS FOR INTEGRATION OF ENERGY
STORAGE DEVICES INTO AN ELECTRIC UTILITY DISTRIBUTION SYSTEM

Voltage (line-to-line), V	13 800±2 percent
Frequency, Hz	60±0.1
Reactive power exchange with alternating-current system, MVAR	±2
Harmonics, percent:	
Plus maximum single voltage	<1
Plus maximum total voltage	<3
Radio interference at 1 MHz, μ V	<100
Audible (adjusted) noise at property line, dBA	<48
Basic impulse insulation level, kV:	
BIL	110
Plus surge arrestors	10
Short-circuit current limit, percent of rated current	<110

TABLE 9. - BREAK-EVEN CAPITAL COST RANGE FOR BATTERY ENERGY
STORAGE SYSTEMS IN PEAKING DUTY

Annual operating time, h	Nominal battery discharge capacity, h	Near-term (1976-85) lead- acid battery	Intermediate-term (1985-2000) advanced battery
		Break-even capital cost, \$/kW	
400	2	50 to 120	140 to 240
1000	5	50 to 230	210 to 440
2000	10	50 to 410	310 to 790

TABLE 10. - BREAK-EVEN CAPITAL COST RANGE FOR BATTERY ENERGY
STORAGE SYSTEMS IN INTERMEDIATE DUTY

Annual operating time, h	Nominal battery discharge capacity, h	Near-term (1976-85) lead- acid battery	Intermediate-term (1985-2000) advanced battery
		Break-even capital cost, \$/kW	
2500	10	20 to 430	330 to 830
3000	12	0 to 490	350 to 950
4000	15	-40 to 620	390 to 1190

are ranges of duty-cycle parameters, tie-in voltage and power levels, electrical interface requirements, and break-even cost goals.

VI. HYDRODYNAMICS

The effort in the area of hydrodynamics has been to evaluate the effect on cell performance of the redox reactant flow characteristics and the cell design parameters. The work performed was mainly experimental, with some supporting analytical studies. The Fe/Ti redox couple pair was used in all the tests. The baseline cell configuration consisted of a carbon cloth electrode flush against each side of a membrane, and a grooved reactant flow plate adjacent to each cloth electrode. The flow plates, which also served as current collectors, were wax-impregnated graphite plates with 0.32-centimeter (1/8-in.-) deep machined flow grooves separated by 0.32-centimeter (1/8-in.) lands.

Five plates were fabricated having, respectively, the following number and width of grooves:

Number of grooves	Width	
	cm	in.
3	1.27	1/2
5	.64	1/4
7	.32	1/8
10	.16	1/16
12	.08	1/32

Each flow groove traced a block-S-shaped path across the 14-centimeter (5.5-in.) by 14-centimeter (5.5-in.) electrode surface. The apparatus used in the experiments is shown in figure 18.

The first screening tests consisted of measuring constant-current discharge performance while maintaining the reactant flow rate and the plate configuration constant on one side of the cell and varying flow rate and plate configuration on the other side. In all cases the cell response was

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Figure 18. - Experimental set-up for hydrodynamics studies.

sluggish when going from open circuit to load. Also, performance was very poor at reactant flow rates that were, though low, still five to ten times greater than the stoichiometric requirement. This latter effect was predicted by a laminar flow model which indicated severe reactant depletion in the diffusion boundary layer when the bulk reactant concentration was as low as 1 M. The use of reference electrodes revealed that the sluggish cell response was associated almost completely with the titanium half-cell. Several cell modifications to induce flow turbulence or to make the electrodes a flowthrough type were evaluated:

- (1) Baffling the reactant flow repeatedly through the cloth electrode
- (2) Reducing the flow groove depth to 0.08 centimeter (1/32 in.)
- (3) Placing turbulence-promoters in the flow grooves

(4) Removing the cloth electrodes and filling the flow grooves with graphite chips or strips of graphite felt. Of these modifications, the first and fourth, which resulted in flowthrough electrodes, were particularly effective in permitting low-flow-rate operation. The flowthrough electrodes also virtually eliminated the sluggish cell response characteristic. The results for the final set of tests are shown in figure 19. These curves illustrate the advantage of using concentrated reactant solutions and flowthrough electrodes.

Upon DOE's programmatic direction, further work under this effort has been postponed for the present, in order to concentrate on other issues.

VII. FACILITY PREPARATION

Early planning for the Lewis redox program called for a multipronged approach to the development of a functional redox system. One aspect of this approach was long-term testing of scaled-up redox cells. It was decided that a new facility should be prepared for this testing, permitting unattended operation of cells for extended periods. The facility was to be capable of controlling the simultaneous testing of six redox cells or cell stacks. The facility (funded by NASA) has been completed, along with the first of the six test stands. A 929-square-centimeter (1-ft^2) cell was operated for several days to check out the test stand, the associated control subsystems, and the

Figure 19. - Effect of reactant flow rate and concentration and electrode type on redox cell performance.

data management subsystem. The facility was then placed in a standby condition because of program redirection by DOE, calling for the postponement of scale-up and life-testing work.

The test facility design consists of three major subsystems: the individual test stands, the test control subsystem, and the data acquisition/management subsystem. The physical layout of the facility, shown in figure 20, consists of a test area and an adjacent control room.

The individual test stands contain the pumps, flow controllers, sensors, power supplies, load-profile controllers, power conditioning equipment, and tankage necessary to support a given test. The partially completed prototype test stand is shown in figure 21. The test control subsystem consists of the logic circuits and switching capabilities necessary to sequence normal cell startup and shutdown procedures, to respond to unprogrammed operation perturbations, and to execute emergency shutdown steps. The data acquisition/management subsystem configuration includes a minicomputer, microcomputer, data collector, multiplexer, typewriter, cathode-ray tube, and associated keyboards. The minicomputer controls the flow of data to data storage for subsequent analysis on the Lewis central computer. It also converts data to engineering units for display in the control room, executes required real-time calculations, does continuous limit-checks on the test data, and initiates emergency shutdown in case of test failure. The microcomputer serves as the interface between the minicomputer and the test facility. It controls the flow of data in both directions and generates hard-copy and/or CRT displays in the control room. Final data reduction and output are accomplished after data transfer from the data storage system to the Lewis central computing facility.

All equipment operated satisfactorily during the shakedown tests.

Figure 20. - Floor plan for redox cell/stack test facility.

Figure 21. - Partially-completed redox cell/stack test stand.

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