REDOX FLOW CELL DEVELOPMENT AND DEMONSTRATION PROJECT

Lewis Research Center, National Aeronautics and Space Administration, Cleveland, OH 44135 (U.S.A.)

The intent of this effort is to develop and demonstrate a Redox Flow System of sufficient energy storage capacity to provide useful operating experience and preliminary cost data as basic input for the design and construction of commercial systems for solar and utility storage applications. The short-term objective is to meet specified performance levels for membranes, electrodes, and single cells after extended periods of cycle testing, and to exceed the short stack power capabilities attained during the previous project period.

During 1979, four related areas of effort were considered. These are in the areas of membranes, electrodes, and single cell and stack testing. Membrane tasks include further reduction and stabilization of membrane resistivity while maintaining high selectivity. Electrode tasks involve increasing the rates of chromium electro-oxidation and electro-reduction, and reducing the rate of hydrogen evolution on charge. Single cell and stack testing concentrates on validating technology advances leading to improvements of amphour efficiency, watt-hour efficiency, and current density.

(1) Membranes have advanced to the point where they will meet system requirements for solar storage applications and are within a factor of two or three of any system requirements for electric utility load leveling. The highly selective anion exchange membrane that was developed at Ionics, Inc. for redox applications almost completely prohibits the passage of the iron and chromium ions, and yet allows easy passage of chloride and hydrogen ions. These advanced membranes can be made using low-cost, mass production techniques.

(2) Reactant solutions were further evaluated and the iron/chromium redox couple was confirmed as the best choice. Reactant solutions are currently 1M in iron or chromium chloride and 2N in hydrochloric acid.

(3) Chromium electrode performance is no longer a problem and meets efficiency and rate requirements for solar storage systems, and requires only modest further improvement in rate of charge for utility requirements. This electrode uses an inexpensive, easily applied catalyst containing very small amounts of gold and lead which was developed by Giner, Inc. for this purpose. A technique for incorporating the catalyst into the porous electrode was developed and >3000 deep charge-discharge cycles with less than 10% loss of performance was demonstrated. Through refinements in catalyst formulation, further progress in suppression of the very small coevolution of hydrogen on charge and increase of the rate of charge in a practical cell is being made.

(4) Redox cell (0.33 ft^2) performance has reached 0.9 V at 30 A per square foot at 50% depth of discharge after 1000 h of operation. Power densities of greater than 60 W per square foot have been achieved.

(5) The iron-hydrogen rebalance cell was developed and incorporated into 0.33 ft² hardware. This allows the small amount of hydrogen evolved in the charging mode to be used automatically to keep the system in charge balance. In this way system capacity remains invariant with cycling except for the very slow loss due to cross diffusion.

(6) Construction methods have been refined for building up the redox system power conversion unit (or stack). It is made up of cells connected together in parallel hydraulically, and in series electrically. The common reactive fluids for all cells enable the stack to be treated as a single operating unit, rather than a collection of many separate cells. This greatly enhances (a) the ability to keep the system in proper charge balance and (b) the capability of internal voltage regulation.

(7) The five-cell stacks tested recently have been 99% A h efficient and 75% W h efficient at 20 A/ft². It is estimated that only a 25% capacity loss could occur in a span of 25 - 30 years based on current membrane cross diffusion characteristics.

(8) Incorporation of an open circuit voltage cell for monitoring the state of charge of the two reactant solutions and of trim cells for internal regulation has been accomplished in 0.33 ft² stack hardware.

(9) Significant reduction in shunt currents has been accomplished by placing insulators in the ports of the bipolar plates and membranes in stacks. Shunt currents can now be minimized within acceptable limits for system application.

(10) Preliminary cost studies for redox systems have been completed assuming a reasonable (75%) reduction in the price of chromium chemicals (verified by producers) and reasonable rates of production using the 1979 prices of existing equipment including inverter. The system cost is 163/kW +20/kW h. The upper limit system cost without any chromium cost reduction is 325/kW + 51/kW h. More refined cost studies are underway under contract to United Technologies Corporation.

During 1980, a System Development effort will be initiated, leading to a prototype multikilowatt solar photovoltaic storage system in field tests by 1983 and megawatt utility storage modules for BEST or other utility facilities by 1985.

Recent publications

- 1 G. Ciprios, Redox bulk energy storage system study by Exxon Research and Engineering Company, Corrigendum — Final Report, NASA Contract NAS3-19776, February 28, 1978.
- 2 R. F. Gahn, Supply of reactants for redox bulk energy storage systems, DOE/NASA/ 1002/78/1, September, 1978.

- 3 L. H. Thaller, Redox flow cell energy storage systems, DOE/NASA/1002/79/3, June 4 6, 1979.
- 4 L. H. Thaller, Recent advances in redox flow cell storage systems, DOE/NASA/1002/ 79/4, August 5 - 10, 1979.

RECHARGEABLE ALKALINE ZINC/FERRO-FERRICYANIDE HYBRID REDOX BATTERY

Lockheed Palo Alto Research Lab., Lockheed Missiles & Space Co., Inc., Palo Alto, CA 94304 (U.S.A.)

The objective of this 12-month contract is to develop and demonstrate the technical feasibility of the zinc/ferro-ferricyanide hybrid redox battery for application to electric utility load leveling and to estimate ROM costs of a 10 - 85 MW h system based upon the experimental data developed.

During fiscal year 1978 - 1979 a multifaceted program has been conducted to assess the fundamental feasibility of the LMSC hybrid redox battery. This program consisted of: (1) basic electrochemical screening of potential electrode substrates; (2) determination of the physiochemical characteristics of electrolytes; (3) evaluation of candidate separators; (4) construction of a microcomputer cyclic control system and test stand; (5) half-cell cyclic testing to determine optimal conditions for individual electrode reactions; (6) full-cell cyclic testing to evaluate operational parameters and obtain cycle life data; (7) cost analysis based upon data obtained from the above studies.

The cell configuration, presently under single cell cyclic life testing, based on the screening studies, is as follows:

 $\label{eq:cd/Zn} Cd/Zn \cdot 5N \ NaOH/ \frac{Nafion}{114} / Na_3 Fe(CN)_6 (sat'd) \cdot 5N \ NaOH/Ni.$

The negative electrode is cadmium-plated iron and the positive electrode is porous nickel, with an ion exchange membrane separator. The cell is maintained at 40 °C and exhibits high cell voltage (1.84 V OCV) and electrode reversibility (1.7 V at 35 mA/cm^2 or 60 mW/cm^2). Peak power density is over 4.5 kW/m² with the present cell design. Cycle life testing for the ferroferricyanide redox half-cell stands presently at 740, 4 hour cycles with a constant 90.6% energy efficiency; full-cell cycle life testing stands at 420, 4 hour cycles completed, at a current density of 35 mA/cm^2 , with a statistical mean energy efficiency of 81.1%. Cycle life testing is continuing.