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RECHARGEABLE ALKALINE ZINC/FERRO–FERRICYANIDE HYBRID REDOX BATTERY

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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:

$$\mathrm{Cd/Zn\cdot 5N\ NaOH}/\genfrac{}{}{0pt}{}{\mathrm{Nafion}}{114}/\mathrm{Na_3Fe(CN)_6(sat'd)\cdot 5N\ NaOH/Ni.}$$

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 $\mathrm{mA/cm^2}$ or 60 $\mathrm{mW/cm^2}$). Peak power density is over 4.5 $\mathrm{kW/m^2}$ with the present cell design. Cycle life testing for the ferro–ferricyanide 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 $\mathrm{mA/cm^2}$, with a statistical mean energy efficiency of 81.1%. Cycle life testing is continuing.

A preliminary analysis of capital costs for this system based on a 10 MW - 85 MW h utility bulk energy storage facility, using preproposal data of 70% energy efficiency at a power density of 52.5 mW/cm^2, indicated a total cost of $33/kW h. A cost analysis using present cell parameters is underway. Preliminary computations, using 81% mean energy efficiency at 60 mW/cm^2, would reduce this figure to approximately $30/kW h. A $5/kW h additional cost reduction is projected based upon an estimated 30% reduction in the cost of sodium ferrocyanide for multi-kiloton lot purchases. This would give a cost figure of less than $25/kW h. By comparison, latest cost estimates for equivalent installations of other systems are as follows: lead–acid ($45 - 60/kW h), zinc–chlorine hydrate ($26/kW h), and zinc–bromine (<$50/kW h).

The tasks for the last quarter of 1979 were completion of half-cell and full-cell cycle tests and a revised capital cost analysis, based upon present data. The results of the present study show the feasibility of the zinc–ferricyanide hybrid redox battery, and a follow-on proposal has been written for a 1980 program which involves: continued cycle life testing; additional studies of candidate electrode substrate materials; photomicroscopic examination, *in situ*, of the zinc electrode during charge and discharge; evaluation of separator materials; investigation of shunt current distributions on a 5 cell battery; an updating of the cost analysis. Technical objectives are: the demonstration of a 200 mA h/cm^2 zinc half cell; attainment of a power density of 100 mW/cm^2 at 70% energy efficiency; definition of the kinetics and mechanism of redox electrolyte instability.

Major technical problems requiring resolution are: (1) to obtain improved zinc electrodeposits, to provide a capacity of 200 mA h/cm^2. The character of the electrodeposits will be optimized using photomicroscopic techniques, *in situ*, to observe the effects of changes in flow geometry, current density, and electrolyte additives, to obtain consistently dense crystalline deposits over many charge/discharge cycles; (2) to obtain improved stability of the redox electrolyte. In the present study it has been determined that decomposition proceeds slowly through abstraction of cyanide to form a pentacyanoaquo iron species, either +2 or +3. Re-ligation of CN^- has been demonstrated with sodium cyanide addition with consequent restoration of electrochemical capacity. The kinetics of instability will be studied using analytical techniques developed by LMSC and various methods of stabilizing or re-ligating the electrolyte will be evaluated using this technique. In addition, it is realized that certain heavy metals readily abstract CN^- from ferro/ferricyanide, thus the catalytic abstraction by porous nickel may be a possible precursor, and other substrates, such as porous carbon, will be evaluated as substitutes.