NASA TECHNICAL MEMORANDUM

NASA TM X-3359

NASA TM X-3359

MODEL FOR CALCULATING ELECTROLYTIC SHUNT PATH LOSSES IN LARGE ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS

Paul R. Prokopius

Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • APRIL 1976

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM X-3359		

4. Title and Subtitle	5. Report Date
MODEL FOR CALCULATING ELECTROLYTIC SHUNT PATH LOSSES IN LARGE ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS	April 1976
	6. Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Paul R. Prokopius	E-8501
	10. Work Unit No.
9. Performing Organization Name and Address	506-23
Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Memorandum
National Aeronautics and Space Administration Washington, D. C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Generalized analysis and solution techniques were developed to evaluate the shunt power losses in electrochemical systems designed with a common or circulating electrolyte supply. Sample data are presented for a hypothetical bulk energy storage redox system, and the general applicability of the analysis technique is discussed.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Electrochemical energy conversion Electrolytic shunt currents Circuit analog Computerized solution technique	Unclassified - unlimited STAR Category 44

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	13	$3.25

* For sale by the National Technical Information Service, Springfield, Virginia 22161

MODEL FOR CALCULATING ELECTROLYTIC SHUNT PATH LOSSES IN LARGE ELECTROCHEMICAL ENERGY CONVERSION SYSTEMS

by Paul R. Prokopius

Lewis Research Center

SUMMARY

The quest for efficient energy conversion techniques may bring about the commercialization of electrochemical energy storage and generation systems. Within this general classification some of the systems may be designed with a common or circulating electrolyte supply. In such systems one of the factors that must be accounted for in the design is the power loss or self-discharge by cell to cell ionic shunt currents. This study addresses this design facet, the objective being to develop a mathematical analysis and solution technique to evaluate the shunt power losses in large electrochemical systems.

Analytical tools consisting of an electrical shunt current circuit analog and a computerized solution technique were devised. This analytical work was done on the redox flow cell, but it is generally applicable in modified form to other systems. Representative data are presented for a sample redox system, and the applicability of this analysis technique to other systems such as fuel cells or fluid flow networks is discussed.

INTRODUCTION

A design concept of many electrochemical energy conversion systems is to use a circulating or common electrolyte supply. Representative systems past and present in which this concept is employed are as follows:

(1) Hydrazine - hydrogen peroxide fuel cells (Alsthom Company)

(2) Low temperature alkaline fuel cell (Union Carbide)

(3) Lithium - seawater battery (Lockheed Company)

(4) Bulk energy storage redox (NASA-Lewis Research Center)

The reasons for designing a system with a circulating electrolyte are varied. These include using the flowing electrolyte stream for a reactant delivery system as in the hydrazine fuel cells and redox flow cells, a heat and water removal medium as in the alkaline cells, or a reactant control parameter as in the lithium-seawater battery. Though the individual design reasons vary, a parameter common to all systems which employ a circulating electrolyte is the power loss or self-discharge through cell to cell ionic shunt currents.

This shunt loss characteristic needs to be considered in any system design; however, most cases in the past did not require an indepth analysis. A common approach was to extrapolate basic shunt loss calculations to the size of the systems under consideration. In the simplest sense this extrapolation was made from single shunt loop loss calculations or from small stack analyses. For the most part, this type of analysis was sufficient for the low voltage systems (i. e., low shunt current driving voltage) built for unique applications - space, underwater, etc. In this type of system, while operating efficiency is an important consideration, design emphasis is placed on system reliability. This is not the case, however, for large terrestrial systems such as bulk storage redox. In this class of systems, design emphasis is placed on conversion efficiency as well as reliability; consequently, the shunt loss characteristic becomes more significant in the system design.

With this background, a study was conducted to develop generalized shunt power loss analyses and solution techniques. An electrical circuit was proposed as an analog model, and a computer program was written with which to do the shunt loss calculations. The computer program was generalized in the sense that by making minor program input modifications virtually any size or type of electrochemical system can be analyzed.

SHUNT CURRENT MODEL DEVELOPMENT

Redox Concept

A redox couple is characterized by a pair of oxidation-reduction reactions in which the ions of the couple remain soluble in their electrolytes in both the reduced and oxidized state. The rechargeable redox flow cell scheme is based on pumping two redox couple solutions through a power conversion unit to alternately charge and discharge the reactant solutions. In a utility bulk storage application the power conversion unit would be coupled with the power network such that the reactant solutions could be charged to store excess off-peak power and discharged to supply the peak power demand. A detailed description of the redox flow cell concept is presented in reference 1.

A general schematic of a two-tank bulk energy storage redox system is shown in figure 1. The main components of this system are the catholyte and anolyte storage tanks, reactant circulating pumps, power conversion unit, and ac to dc and dc to ac power conditioning equipment. The couples chosen for illustration are titanium trichloride/titanium tetrachloride and ferrous/ferric chloride. Their respective charge-discharge reactions are shown on the schematic. In the discharge mode energy stored electrochemically in the electrolyte is converted and supplied on demand to the ac network to which the redox system is connected. Recharging is the reverse process and is accomplished by applying the appropriate voltage across the cell electrodes to drive current in the opposite direction.

A redox system in a utility application would require a cell stack (power conversion unit) which operates in excess of 100 volts. A voltage level of this order of magnitude is needed to attain efficient operation of the high power semiconductors of the ac-dc power conditioners. The couples most commonly considered for application are aqueous solutions. Thus, the practical maximum attainable per cell charge voltage is about 1.2 volts because of the possible electrolysis of the water on charging. Therefore, in terms of stack size, a basic power unit of upwards of 100 series-connected cells would be required to produce the 100-volt minimum. Borrowing design characteristics developed for fuel cells, the redox stack might, for the purposes of this study, be assumed to be assembled in a bipolar configuration; that is, the structural members separating the cells are conductive and provide the series electrical path through the stack. Also, a parallel reactant feed is assumed in which each of the individual cell reactant supply and return lines are paralleled off common manifolds. A schematic of a four-cell redox stack incorporating these two characteristics is shown in figure 2.

Each individual cell of the power conversion unit consists of electrolyte supply chambers through which the reactant solutions are circulated, inert electrodes which serve as current collectors, and an anion-selective ion exchange membrane to separate the electrolytic solutions. In this configuration, the filled electrolyte supply/return lines connected by common manifolds form cell to cell shunt paths that are conductive to ionic currents. Ionic currents are generated and driven through these shunt paths by the cell to cell potential gradients of the stack. These currents represent an internal I^2R power loss or self-discharge characteristic of the stack and thus must be kept to a minimum in any system design. The shunt losses become a system design parameter by virtue of the fact that the resistance of the shunt current paths is a function of the geometry of the electrolyte circulation system and the conductivity of the electrolyte ($R_S = l/GA$ where R_S is the shunt path resistance, l and A are shunt path length and area, and G is electrolytic conductivity). The tradeoff between shunt losses and electrolyte pumping power losses provide a simple example of one of the shunt loss design considerations; that is, the shunt path resistance can be made very large and hence the shunt currents very small by designing the cell with long, small diameter electrolyte feed/return lines. On the other hand, an increase in shunt current resistance accomplished in this manner is accompanied by an increase in electrolyte flow resistance which must be overcome by an increase in pumping power. To properly assess the shunt loss portion of this design tradeoff as well as others involving shunt currents, an analytical technique is needed.

Circuit Analog

For the system just proposed, a circuit analog of the stack current flow paths was devised as an analytical tool with which to do the shunt current analysis. In the analog each cell of the redox stack is represented by an ideal voltage source with an internal series resistance. The internal resistance is the electrical resistance through the cell in the direction of current flow. In each of the electrolyte shunt loops the electrical resistance to the ionic shunt currents is distributed along the path length. However, in the analog circuit these resistances are lumped into passive resistor elements; that is, each of the four electrolyte supply and return taps of each cell is represented by a resistive element as is each manifold segment between any two taps. The complete analog circuit for the four-cell stack of figure 2 is shown in figure 3. The various components are represented as follows: R_i, cell internal resistance; e, ideal cell voltage (open circuit voltage); R_A, anodic feed and exit port resistance; R_C, cathodic feed and exit port resistance; R_{AM}, anode manifold segment resistance; R_{CM}, cathode manifold segment resistance; and R_L, system load resistance. Several assumptions are inherent in the construction of the circuit analogy. First, it was assumed that the only component comprising the cell internal resistance R_i is the membrane resistance to ionic current flow. The resistance through the cell electrolyte in the direction of current flow (perpendicular to the electrode) plus that of the inert electrodes and the bipolar cell separator plates are small compared to the membrane resistance and are assumed negligible. Second, in keeping with the lumped parameter approach, the electrolyte in any of the reactant chambers is assumed to be at a uniform potential throughout; that is, the electrolyte discharge gradient from cell inlet to outlet is assumed negligible. As a result of this assumption, an internal phenomenon such as eddy currents generated by the discharge potential gradient across the cell is considered to be a second-order effect and is thus neglected.

The analog circuit, by nature of the system being simulated, is a linear, symmetrical, passive, dc network to which Kirchoff's Law can be applied to determine the shunt current losses. Each cell except the two end cells of the stack generate four independent conductive loops which have the cell equivalent circuit as a common element. The end cells generate only two loops by virtue of the fact that the conductive paths from the electrolyte supply to return manifolds are assumed broken in the pump circuit. Thus, the anolyte circuit of the cell on the low voltage end of the stack forms only one set of conductive loops with the anolyte circuit of the adjacent cell. Similarly, on the high voltage end of the stack, the catholyte feed end return lines form only one set of loops with the adjacent cell.

MODEL ANALYSIS

As stated previously, the shunt path analog circuit can be analyzed using Kirchoff's Law. The currents shown on the circuit diagram of figure 3 are the Kirchoff loop currents for the 13 independent loops of the four-cell stack. The currents i_1 to i_{12} represent the shunt loop currents and i_L the loop current for the load circuit. In this network, clockwise current flow was designated as the positive current direction. Equating the sum of the IR voltage drops around each of the Kirchoff loops to the voltage rise across the cell ideal source generates the voltage drop equations for the 13 independent loops. These result in a set of 13 simultaneous algebraic equations to be solved for the 13 unknown loop currents. The loop currents thus identify the currents flowing through the various elements of the electrolytic leakage paths. In some instances the loop current itself defines a leakage or shunt current factor. This occurs whenever the component in question is not in common with any other loop. The currents which are not determined directly are defined by a difference in loop currents such as $(i_2 - i_6)$ which defines the leakage current flowing in the anolyte feed line to cell two. The leakage current through each individual resistive component is needed to calculate the power loss in each component. The individual component power losses can then be summed to determine the total shunt current power loss of the stack.

For a redox stack of N cells with the stack configuration shown in figure 2, the expression $4(N-1)+1$ defines the number of Kirchoff loop equations in the circuit analogy. From this it is obvious that for any commercial sized stack, which would undoubtedly involve hundreds of equations, a computerized analysis is necessary.

Of the many direct, iterative, or statistical methods of solving systems of linear equations, Crout's method appears to be well suited to this application in terms of computational and computer storage efficiency. In this method a matrix is constructed using the coefficients and independent variables of the Kirchoff equations. This coefficient matrix is manipulated on a term by term basis to obtain a derived matrix from which the equations' solutions can be obtained. The manipulation is such that as the various terms are being determined for the derived matrix, the terms of the original coefficient matrix need not be retained. Thus, only one matrix array need be allocated in the computer storage system. Also, because of the symmetry of the circuit being analyzed and the limited degree of commonality from loop to loop, the resultant equation matrix is largely symmetrical with only a few nonzero terms on either side of the major diagonal. Again, Crout's method lends itself well in taking advantage of this symmetry and the large blocks of zero terms. The resultant effect is that a very large number of simultaneous equations can be handled with a very small array.

The mechanics of the computational method may be best explained by an example. Given are three equations in the three unknowns, x_1, x_2, x_3:

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = a_{14}$$

$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = a_{24}$$

$$a_{31}x_1 + a_{32}x_2 + a_{33}x_3 = a_{34}$$

The coefficients and dependent variables of these equations form the matrix

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \end{vmatrix}$$

The various terms of this matrix are operated on to obtain a derived matrix

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \end{vmatrix}$$

The expressions used in calculating the terms of the derived matrix are as follows:

$$A_{ii} = a_{ii} - \sum_{K=1}^{i-1} A_{iK}A_{Ki}$$

$$A_{ij} = a_{ij} - \sum_{K=1}^{j-1} A_{iK}A_{Kj} \qquad \text{(if } i > j\text{)}$$

$$A_{ij} = \left[a_{ij} - \sum_{K=1}^{i-1} A_{iK}A_{Kj}\right]\frac{1}{A_{ii}} \qquad \text{(if } i < j\text{)}$$

Once the derived matrix is obtained, the solutions to the n unknown variables of the original equations are calculated from

$$x_n = A_{n,\, n+1}$$

$$x_i = A_{i,n+1} - \sum_{K=i+1}^{n} A_{iK} x_K \quad \left[i = (n - 1) \rightarrow 1\right]$$

A computer program (Fortran IV) using Crout's method was written for the redox configuration shown in figure 2. The program was written in a generalized form so that any sized stack of this particular configuration could be run directly or a variation from this configuration could be accommodated by a minimal modification in the program input relations. The actual stack size limitation is determined by the array storage limitation of the machine on which the program is being run.

The program was written so that the only inputs required are the basic stack parameters such as the number of cells, the ideal cell voltage, and the various resistance values. From these data the equation and derived matrices are generated by the program and the loop currents are determined. In constructing the equation matrix, the two loops on either end of the stack plus the load circuit generate unique Kirchoff equations; however, the interior loop equations along any one manifold are repetative, the only difference being an indexing of the current subscripts from loop to loop. Thus, the recursion equations for these interior loops were derived and programmed to facilitate generating the equation matrix. This matrix takes on a general form in which (1) all the terms within the body of the matrix are grouped in four locations to either side of the major diagonal, (2) all the positions in the last two columns are filled, and (3) the last row is completely filled. Read into a computer in its entirety, an equation matrix for just a 50-cell redox stack would occupy 38,612 storage locations, a number which far exceeds the storage capacity of many machines. A characteristic of the Crout computational technique is that the occurrence of zero in any location of the equation matrix will be duplicated by a zero term in the corresponding location of the derived matrix. This characteristic was used to expand the computational capacity of the program by eliminating all calculations involving zero terms of the equation matrix. The exception to this is the last row of the matrix in which each location is occupied by a nonzero term. This was handled as a special case in the logic by treating it as a single row matrix. In effect, the main body of the matrix was compressed from [4(no. of cells - 1) + 2] columns to only 11 columns in width. This width reduction logic was, by necessity, carried through the construction of the derived matrix and the computation of the results.

To illustrate some of the general shunt current characteristics of a redox stack and to demonstrate the operation of the program, a hypothetical cell and stack design were assumed. The parameters that were used in this exercise are as follows:

Electrolyte solutions:

(Iron) 2M $FeCl_3$ in 0.5N HCl

(Titanium) 2M $TiCl_3$ in 6N HCl

Cell and stack geometry:

- Active cell area, 2 ft^2
- Manifold to cell electrolyte feed and exit tubes, 1/8 in. i. d., 6 in. long
- Supply and return manifolds, 3/4 in. i. d.
- Cell thickness, 0. 16 in.
- Membrane thickness, 0. 020 in.
- Stack size, 96 cells
- Supply and return manifold lengths, 15. 4 in.

Electrical parameters:

- Iron couple specific conductance, 0. 151 $(\Omega\text{-cm})^{-1}$
- Titanium couple specific conductance, 0. 165 $(\Omega\text{-cm})^{-1}$
- Electrolyte feed and exit line resistance, 1205 Ω
- Cell to cell manifold resistance, 1. 0 Ω
- Membrane resistivity, 67 Ω-cm
- Ideal cell voltage, 0. 7 V
- Load resistance, 0. 144 Ω

The system load resistance was set such that the stack would supply approximately 200 amperes to the load circuit. For the anolyte feed manifold of a 96-cell stack, the shunt currents in the cell to cell manifold sections as calculated by the program varied from 7. 2 milliamperes for the end cells to 152 milliamperes in the center of the stack. The corresponding cell to cell voltage distribution varies from 0. 2890 volt for the end cells to 0. 2878 volt in the stack center. These distributions are shown in figure 4. The power delivered to the load by this 96-cell system is 6. 078 kilowatts, while the total shunt power loss was calculated to be only 11. 75 watts. This small shunt loss value was not unexpected since the electrolyte system was designed with a large feed line resistance.

The system shunt power loss was found to increase exponentially with stack size. This characteristic is illustrated in figure 5 for the cell design assumed previously. The one component which is a tempering element in the slope of the exponential characteristic is the cell to cell manifold resistance since this represents an incremental resistance added to the circuit with each cell.

The validity of the computer program was verified by comparing results calculated with the program to those obtained from a standard simultaneous equation computer subroutine. Because of the size limitation of the standard routine this comparison was done for a relatively small stack. However, because of the recursive nature of the method programmed, validity can justifiably be assumed for any sized stack.

CONCLUDING REMARKS

The analysis technique described previously is not limited to the shunt current analysis of the parallel feed, bipolar redox system. Examples of other possible uses include shunt current analyses of redox systems with other feed configurations or shunt current analyses of fuel cell systems employing circulating electrolytes. It could also be used for hydrodynamic analyses of flow networks such as the redox or fuel cell electrolyte supply systems. Each of these types of systems generate a modified form of the circuit analogy that was developed for the two loop redox system. For example, the network analog for a fuel cell stack with a circulating electrolyte would consist of only two sets of Kirchoff loops instead of the four sets of the redox system. As another example, the network analog defining the fluid flow distribution of an electrolyte supply system would be represented by just a single set of Kirchoff loops. In this case the resistive elements of the redox analog would represent fluid flow resistances. The voltage sources would be omitted from the individual loops, but a voltage source representing the electrolyte pump pressure would be inserted in the load circuit.

To accomplish a change in the programmed analysis from a four loop set to a two loop set network would merely require the omission of two sets of Kirchoff equations in constructing the equation matrix. Equally simple is the elimination or addition of elements such as loop voltage sources since the equation matrix is constructed with the use of recursion equations.

The general ease of program modification and the high degree of similarity between systems could be advantageous in doing system design studies. For example, the redox shunt current and electrolyte flow analyses could easily be combined in an iterative program for doing design optimization studies.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 15, 1975,
506-23.

REFERENCE

1. Thaller, L. H.: Electrically Rechargeable Redox Flow Cells. 9th Intersociety Energy Conversion Engineering Conference, Am. Soc. Mech. Engrs., 1974, pp. 924-928.

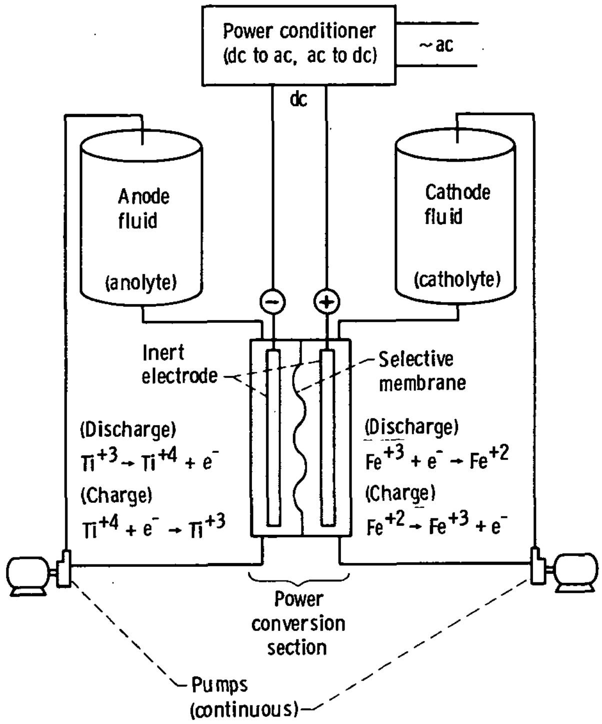

Figure 1. - Two tank electrically rechargeable redox flow cell.

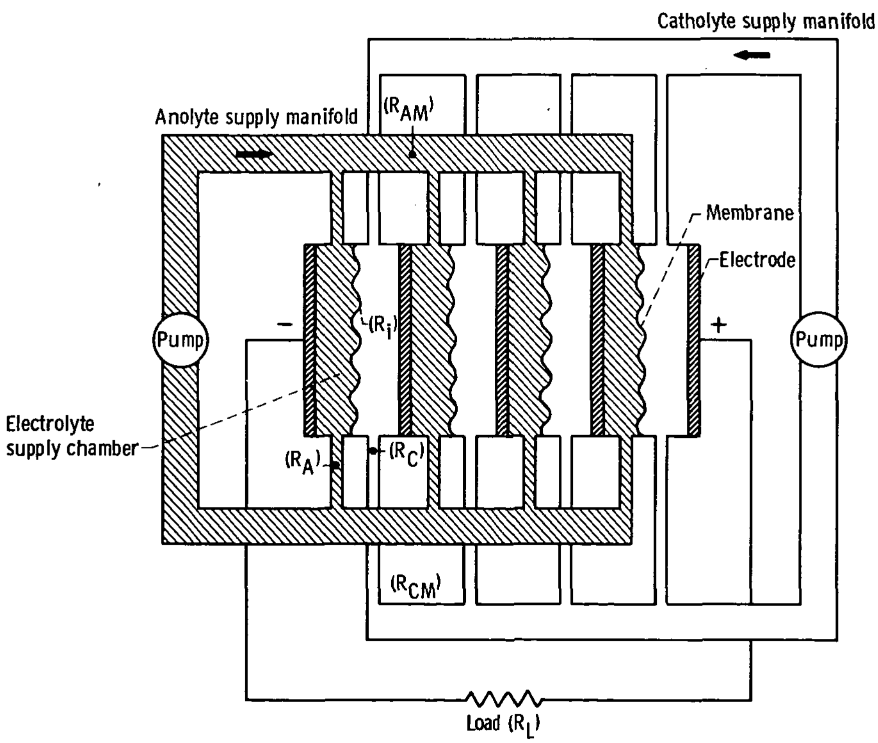

Figure 2. - Four cell redox system flow schematic.

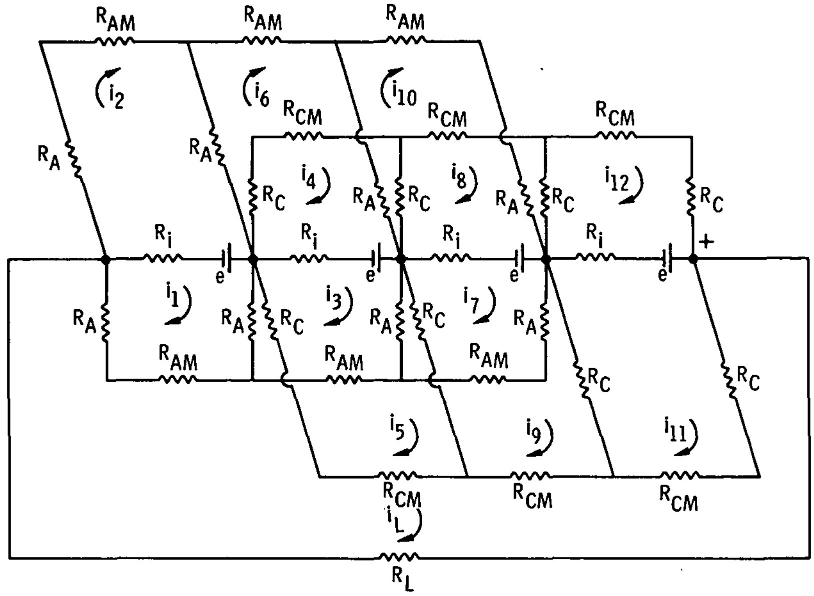

Figure 3. - Four cell redox system electrical analog.

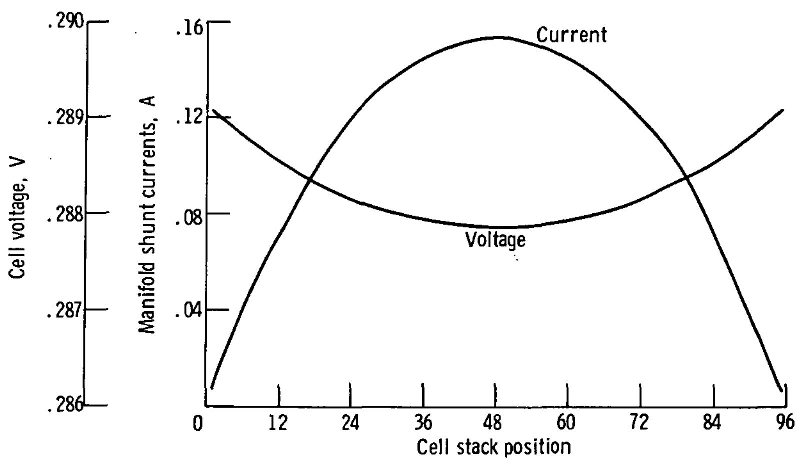

Figure 4. - Cell to cell shunt current and voltage distributions.

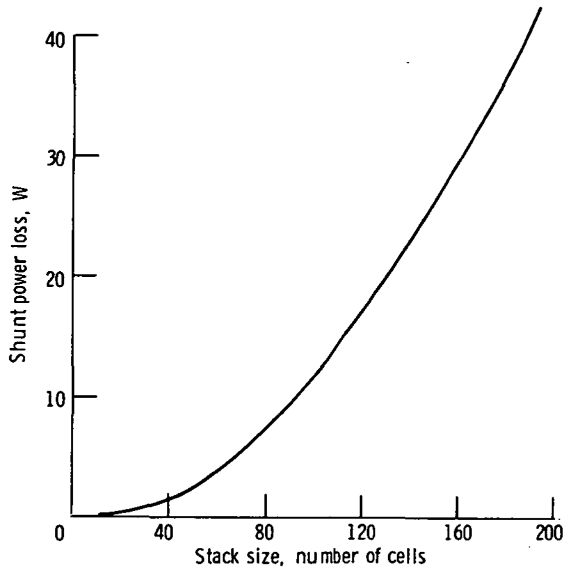

Figure 5. - Stack shunt power loss as a function of stack size.

NASA-Langley, 1976 E-8501