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SUMMARY

An electrochemical rebalance cell for maintaining electrochemical balance, at the system level, of the acidified aqueous iron chloride and chromium chloride reactant solutions in the NASA Redox energy storage system was constructed and evaluated. Technology from both fuel cell and Redox cell work was used to develop the rebalance cell.

Polarization tests were conducted on the rebalance cell by reducing the ferric ion in the 310-cm^2 (0.33-ft^2) cell through the use of various hydrogen half-cell configurations. A configuration containing reticulated vitreous carbon foam, a platinum catalyzed electrode, and a Kynol wick operated with reversible electrode reactions, low internal resistance, and reproducible voltage-current relationships at current densities to 54 mA/cm^2 (50 A/ft^2). The results of tests with this configuration are discussed in this report.

Gradual transfer of iron chloride to the hydrogen side caused flooding of the hydrogen cavity and an unstable voltage at high current densities. Occasional maintenance of the cell was necessary to recover its performance. The maintenance procedure consisted of filling the hydrogen cavity with 1 M sulfuric acid and then draining the cavity.

The rebalance cell was also demonstrated in the form of a five-cell stack with parallel iron solution flow. Tests were conducted with hydrogen gas flow in parallel and in series. Series flow is preferred to ensure hydrogen flow to all cells.

The ability of the rebalance cell to reduce other aqueous metal ions, such as Cu(II), V(V), Cr(III), and Ti(IV), to a lower state of oxidation without the aid of a chemical reducing agent was also demonstrated.

INTRODUCTION

The National Aeronautics and Space Administration has been developing the Redox system (ref. 1), an electrochemical storage concept that functions as a rechargeable battery. The system, shown in figure 1, uses two fully soluble reactant solutions (i.e., acidified iron chloride and chromium chloride), which are stored in separate tanks and circulated through one or more Redox cells. In each cell an anion exchange membrane separates the two cation species but allows chloride transfer.

Electrochemical imbalance of the reactant solutions results from minor side reactions, such as the coevolution of hydrogen gas at the negative electrode during chromium charging and chromous and ferrous oxidation by air intrusion into the system. As a consequence the system cannot attain 100 percent coulombic efficiency on each cycle. Because the net effect is cumulative, corrective action must be taken to maintain the system storage capacity.

By far the most significant side reaction is hydrogen evolution at the chromium electrode during the charge portion of the cycle. The charging reaction that occurs at the chromium electrode is

$$Cr^{+3} + e^- \longrightarrow Cr^{+2}$$

The undesirable side reaction is

$$H^+ + e^- \longrightarrow 1/2\ H_2(g)$$

The singular reaction at the iron electrode is

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-$$

The cumulative effects of hydrogen evolution are thus twofold; first, the ferric ion concentration exceeds the chromous ion concentration; second, a commensurate amount of hydrogen gas is evolved. It should be emphasized that with the high-quality chromium electrodes now developed the associated loss is less than 2 percent of the charge on each cycle. These undesirable reactions result in the gradual divergence (imbalance) in the electrochemical state of charge of the anode solution relative to that of the cathode solution over long periods of time.

Since the individual cells in the NASA Redox system are hydraulically in parallel (fig. 2), all of the cells share common iron and chromium solutions. Thus the rebalance technique can be applied at the system level: all cells are rebalanced simultaneously. As a result of in-house studies at NASA Lewis, a rebalance cell has been designed and tested (ref. 2) for the purpose of keeping the Redox system in electrochemical balance. This electrochemical rebalance cell can also be used to reduce other cationic species in aqueous solution without adding another reducing ion such as with a Jones reductor. This report describes the construction, performance, and applications of the hydrogen rebalance cell.

EXPERIMENTAL PROCEDURE

Cell Construction

The rebalance cell, a hybrid of a Redox flow cell and a fuel cell, consists of the Redox cell cathode and a fuel cell anode. Its construction is displayed in figure 3. The spontaneous electrode reactions in the cell are

Cathode

$$Fe^{+3} + e^- \longrightarrow Fe^{+2} \qquad E_0 = 0.77\ V$$

Anode

$$1/2\ H_2(g) \longrightarrow H^+ + e^- \qquad E_0 = 0\ V$$

where E_0 is standard electrode potential in volts. These two half-cells are separated by a highly selective anion exchange membrane. The membrane currently used is a copolymer of vinylbenzyl chloride and dimethyl aminoethyl methacrylate designated CD1L-A5-25NP; it is a standard catalyst made by Ionics, Inc., Watertown, Massachusetts (ref. 3). The ion exchange membrane must possess a high bubble pressure and contain small charged pores in order to prevent bulk solution transfer across the membrane with subsequent flooding of the hydrogen half-cell. The Ionics Inc. anion exchange membrane used in a Redox rebalance cell prevents the diffusion of large cations across the membrane to the anode half-cell. Even though the membrane favors anion (Cl^-) exchange, the H^+ cations can also pass through the membrane easily because of their small size and high mobility. The cross-diffusion rate of ferric ions (Fe^{+3}) through this particular membrane is 10 to 15 g/cm^2-hr-M (ref. 3). The cathode half-cell cavity contains a sheet of porous carbon felt. This felt provides a surface for the metal cation reduction reaction.

The anode cavity is illustrated in detail in figure 4. Of the various single-cell designs that have been tested, this particular configuration gave the best results. Hence this report discusses the results of this configuration alone.

The most important component of the anode half-cell is the hydrogen electrode, which consists of a Teflon-coated carbon paper on one side of which platinum black powder catalyst is deposited. The catalyzed side of the electrode, where the electro-oxidation takes place, is slightly hydrophilic and faces the membrane. A sheet of highly absorbent fibrous material, called Kynol, is placed next to the catalyzed side to keep it and the membrane moist. The other side of the electrode, which must have access to the diffusing hydrogen, is hydrophobic.

A sheet of porous, nonwetting carbon material is placed between the hydrogen electrode and the terminal plate. It serves as a current conductor and spacer to allow free flow of the hydrogen to the hydrogen electrode surface. Stiff reticulated vitreous carbon (RVC) foam has been demonstrated to be suitable for this purpose, although other materials have been tested. A thin sheet of compressible carbon felt is placed between the RVC foam and the terminal plate as a spring to compress the components and thus ensure good electrical contact. The anode side of the cell is soaked with sulfuric acid to prevent oxidation of the platinum catalyst. This acid should occasionally be replenished to maintain the performance of the cell. The cell and its assembly are described in detail in the appendix.

Cell Testing Procedure

A schematic diagram of the rebalance cell testing apparatus is shown in figure 5. A dc power supply was used to pass current through the cell. Standard high-impedance digital voltmeters were used to measure cell voltage and current flow through the shunt. The cathode electrolyte was pumped from a 2-liter reservoir to the cell. The reduced iron solution was returned to the same reservoir. The reservoir was left open to the air so that it could reoxidize. Hydrogen was supplied to the anode side of the cell by a hydrogen generator or pressurized tank. A positive flow of hydrogen at atmospheric pressure was maintained in the cell during discharge. Polarization measurements were made at various currents. The internal resistance of the cell was measured by using a 1-kHz ac impedance bridge. The cell voltage was measured at a given current as soon as it reached a steady-state value, generally in about 15 sec. The current was increased in increments and the voltage was recorded until it reached zero. These voltage measurements were plotted on a graph of voltage versus current density. The slope of the curve was in part a measure of the internal resistance of the cell, and the electrochemical activity of the electrode was determined from the linearity.

RESULTS

A typical polarization curve for a single 310-cm^2 (0.33-ft^2) iron-hydrogen rebalance cell is displayed in figure 6. This curve approaches a straight line, indicating a nearly reversible electrochemical reaction. The resistance measured on the impedance bridge was 0.028 ohm; the mean slope of the current-voltage curve was 0.035 ohm. For an ideal cell the slope is equal to the open-circuit resistance measured on the bridge. However, because of possible contact resistance effects, mass transport effects, and other polarization effects, the slope indicated a greater internal resistance. The cell was operated at current densities as high as 54 mA/cm^2 (50 A/ft^2) at positive voltages.

Gradual transfer of iron chloride solution across the membrane to the hydrogen side caused hydrogen electrode flooding and unstable voltages, particularly at high currents. Thus occasional maintenance of the cell was required. The performance was recovered by filling the anode cavity with 1 M sulfuric acid. The acid was kept in the cell for a few minutes; then the excess acid was forced out of the cell by setting the cell in a vertical position and blowing nitrogen gas through the anode cavity. The configuration discussed above operated for a month without this maintenance procedure.

Two multicell rebalance stacks made of five 310-cm^2 (0.33-ft^2) cells were built and tested. The anode half-cell configuration differed slightly from the design discussed earlier in that it used a single stiff sheet of carbon felt, called Thornel, in place of the RVC foam and compressible felt. In the first stack the iron solution and the hydrogen gas flow were in parallel through the anode cavities via common inlet and outlet manifolds. The second stack also had parallel iron solution flow, but the hydrogen gas flow was in series (i.e., the same gas flowed through all five cells). The cells were connected electrically in series in both stacks by electrically conductive bipolar plates. The results from the series stack are presented in figure 7. Although the results of both stacks were similar, the series hydrogen flow design is preferred since this design ensures that all of the cells receive hydrogen. The parallel hydrogen flow approach may allow one or more cells to be plugged with liquid, thus causing the hydrogen gas to bypass these cells. Starvation of hydrogen in any cell causes the cell voltage to become negative and leads to oxidation of the platinum catalyst and chlorine gas evolution. The performance of both five-cell stacks was good initially but decreased significantly with time. Frequent maintenance improved the performance but not to the initial level. No multicell stack has been fabricated using the RVC spacer material.

A 14.5-cm^2 (0.0156-ft^2) rebalance cell was used to reduce metal ions other than iron, such as Cu(II), V(V), Cr(III), and Ti(IV). For the reduction of $CrCl_3$ and $TiCl_4$ a power supply was used to assist the reaction since the reaction potential for titanium is only 0.04 V. Although polarization curves were not attempted, the solutions were reduced at a constant power-supply voltage (1.1 V), letting the current taper down to zero. The polarization curves for vanadium and copper reduction are presented in figure 8. A solution of 0.5 M V_2O_5 (V ion) in 6 N HCl was reduced to the V^{+2} oxidation state. A solution of 1 M CuO (Cu^{+2} ion) in 2 N HCl was reduced to the Cu^{+1} oxidation state. That curves are not linear implies that some chemical or concentration overpotential had influenced the performance of the cell.

CONCLUDING REMARKS

A rebalance cell based on the iron couple (Fe^{+3}/Fe^{+2}) and the hydrogen couple (H_2/H^+) was built and tested as a 310-cm^2 (0.33-ft^2) single cell. A configuration using a reticulated vitreous carbon foam spacer, a platinum catalyzed electrode, and a Kynol wick yielded highly reversible reactions with low internal resistance at current densities to 54 mA/cm^2 (50 A/ft^2).

Two five-cell stacks were also tested: the first, with the hydrogen gas flow in parallel; the second, using series gas flow. These stacks demonstrated the capability of maintaining a Redox system in electrochemical balance.

The rebalance cell technology was also shown to be applicable to other electrochemical reduction reactions. The reduced species of several different metal ion solutions were prepared without adding impurities to the solution.

The flexibility of assembling a single rebalance cell or stacks of cells and the relatively maintenance-free operation make it a useful electrochemical device.

APPENDIX - REBALANCE CELL ASSEMBLY

The rebalance cell can be assembled as a single cell (fig. 3) or a stack of cells (fig. 9) consisting of several single bipolar cells connected electrically in series and hydraulically in parallel. The various structural components of the rebalance cell and their functions were as follows: Steel end-plates, 1.27 cm (1/2 in.) thick, were used for support and rigidity. Machined polyvinylchloride (PVC) end-blocks insulated the cell from the steel end-plates. Polyethylene flow-field frame and gasket frame assemblies provided the cavities for the electrode compartments as well as the inlet and outlet channels and manifolds. Polyethylene was chosen as the gasket material so that the electrode components inside would be compressed sufficiently. This ensured good electrical contact inside the cell cavities. The membrane separated the iron half-cell from the hydrogen half-cell.

The rebalance cell was assembled in the following steps:

(1) A steel end-plate was laid horizontally on two supporting blocks.

(2) A PVC end-block was placed on top of the steel end-plate with all of the holes aligned.

(3) A neoprene rubber gasket frame was sealed to the PVC end block with silicon rubber cement (RTV).

(4) A thin layer of RTV was applied to the neoprene rubber gasket frames around the inlet and outlet ports (primary manifolds) in order to prevent leakage in these areas.

(5) A graphite plate (anode current collector) was then placed on the neoprene rubber gasket frame with the manifold holes aligned properly.

(6) A flow-field frame was glued to the graphite frame with RTV to form the anode cavity.

(7) A sheet of 0.51-mm (20-mil) carbon felt, as received, was inserted into the cavity.

(8) A sheet of RVC foam was placed on the felt.

(9) The hydrogen electrode was placed on the foam with the hydrophobic side facing the RVC foam and aligned in the cavity.

(10) A sheet of Kynol was placed on the hydrogen electrode. This completed the hydrogen side of the cell.

(11) A flow-field frame was glued to the graphite frame (cathode current collector) with RTV to form the cathode cavity.

(12) The iron electrode was placed into the cavity. The felt had been cleaned in boiling aqueous potassium hydroxide for 1 hr and then rinsed thoroughly.

(13) The membrane was placed on the hydrogen electrode.

(14) The cathode half-cell (completed in step 12) was carefully inverted and placed on the membrane without allowing the electrode to fall out of the cavity.

(15) For constructing a multicell stack, steps **6** to 14 were repeated errata 10-26-83 as many times as needed.

(16) The cell was bolted together by using insulated, threaded rods. The cell stack was torqued to approximately 20.5 N-m (180 lb-in) in 2.3-N-m (20-lb-in) increments starting at 11.4-N-m (100-lb-in) torque.

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2. Thaller, L.H.; Electrochemical Cell for Rebalancing Redox Flow System. U.S. Patent No. 4,159,366, June 26, 1979.
3. Ling, J.S., and Charleston, J.; Advances in Membrane Technologies for the NASA Redox Energy Storage System. Presented at the Electrochemical Society Meeting (Hollywood, Florida), Oct. 5-10, 1980.

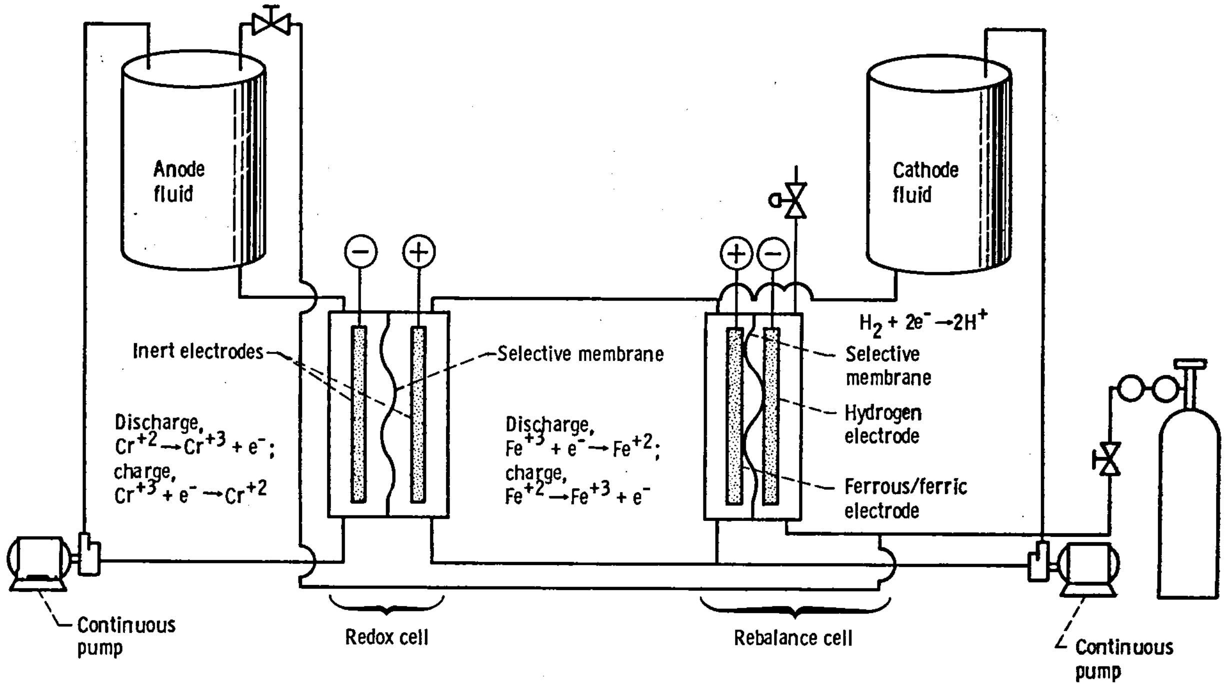

Figure 1. - Redox flow cell with rebalance cell.

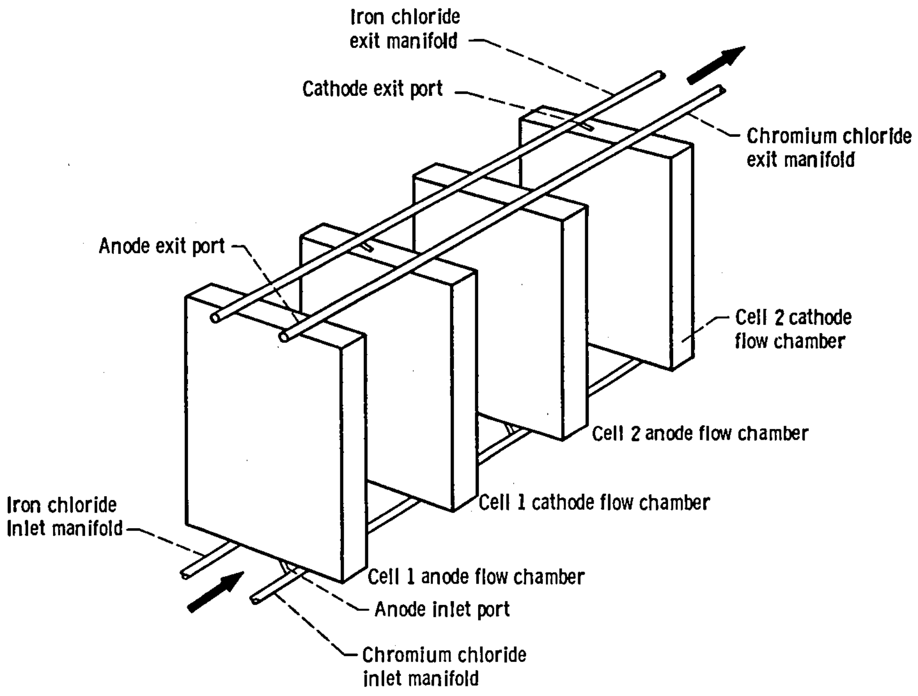

Figure 2. - Hydraulic network in a parallel-flow Redox stack.

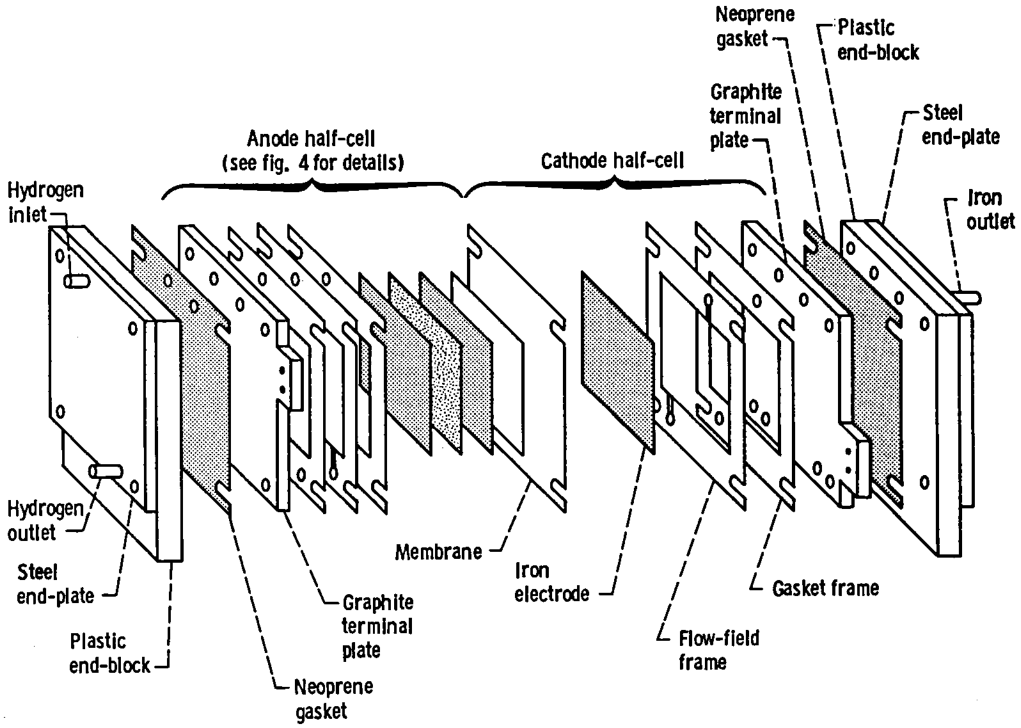

Figure 3. - Construction of rebalance cell.

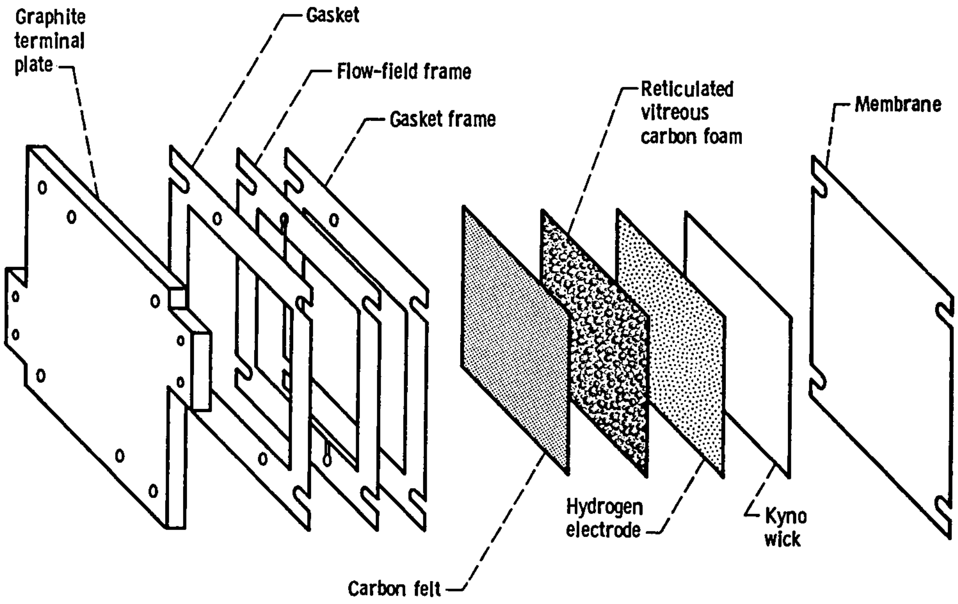

Figure 4. - Detail of anode half-cell.

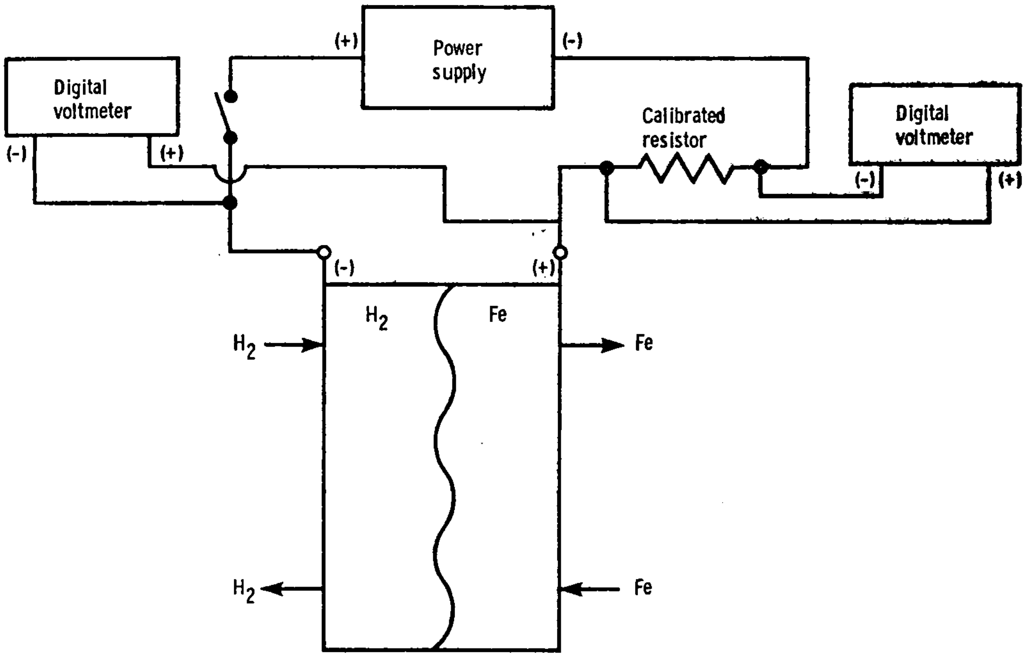

Figure 5. - Schematic diagram of rebalance cell testing apparatus.

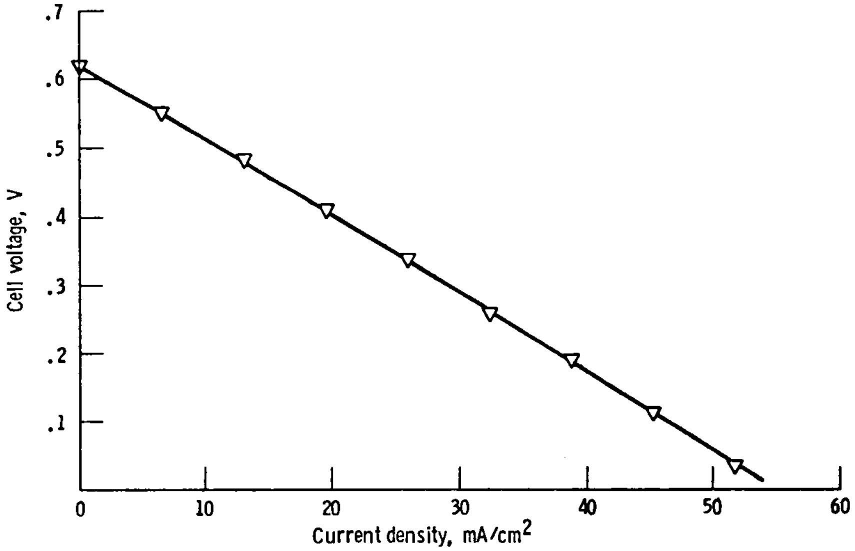

Figure 6. - Polarization curve for single 310-cm^2 (0.33-ft^2) rebalance cell.

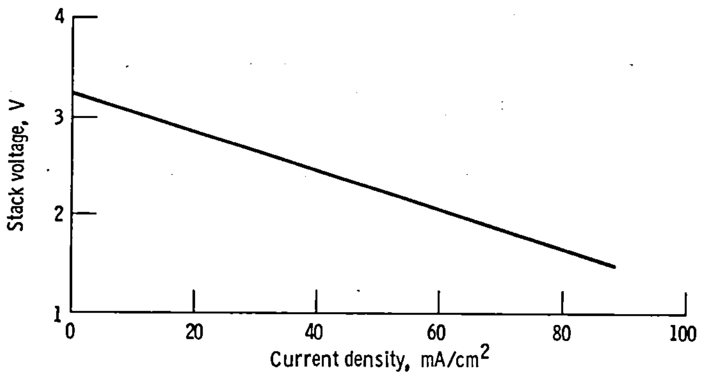

Figure 7. - Performance of five-cell 310-cm^2 (0.33-ft^2) rebalance stack with series hydrogen flow.

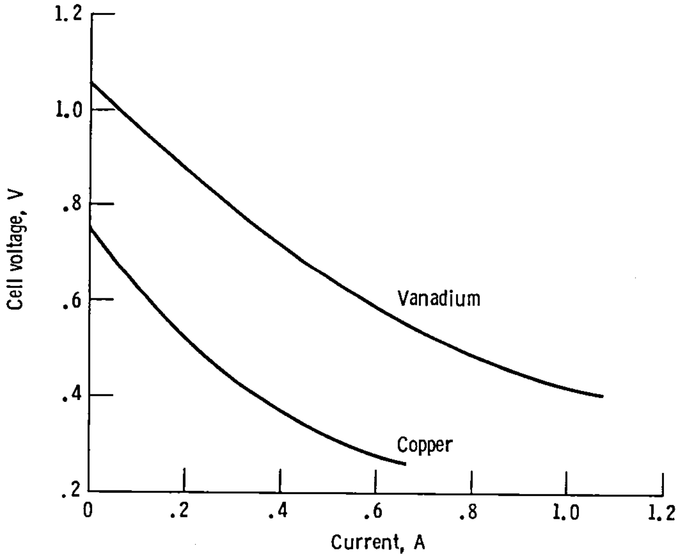

Figure 8. - Polarization curves for reduction of vanadium and copper. Cell area, 14.5 cm^2 (0.0156 ft^2).

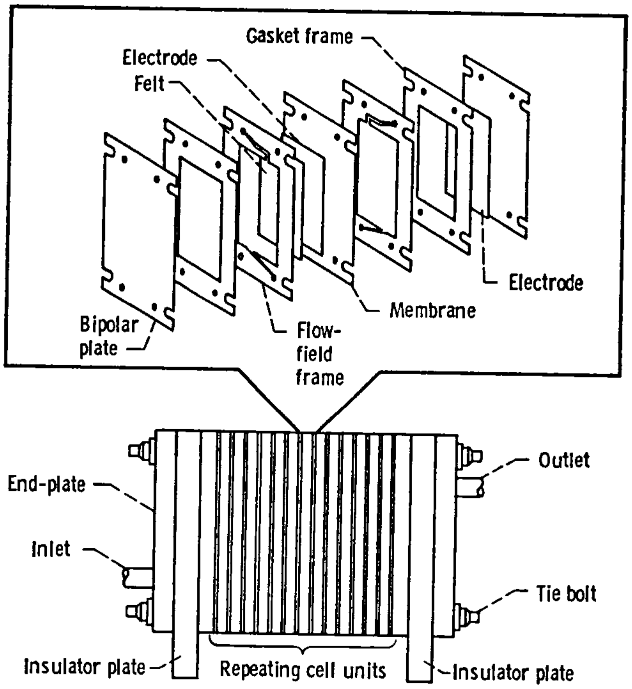

Figure 9. - Rebalance stack and single-cell components.

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16. Abstract

An electrochemical rebalance cell for maintaining electrochemical balance, at the system level, of the acidified aqueous iron chloride and chromium chloride reactant solutions in the NASA Redox energy storage system was constructed and evaluated. The electrochemical reaction for the cathode is $Fe^{+3} + e^- \rightarrow Fe^{+2}$, and that for the anode is $1/2H_2 \rightarrow H^+ + e^-$. The iron (carbon felt) electrode and the hydrogen (platinized carbon) electrode are separated by an anion exchange membrane. The performance of the rebalance cell is discussed as well as the assembly of a single rebalance cell and multicell stacks. Various cell configurations were tested and the results are presented and discussed. The rebalance cell was also used to demonstrate its ability, as a preparative tool, for making high-purity solutions of soluble reduced metal ionic species. Preparations of titanium, copper, vanadium, and chromium ions in acidified solutions were evaluated.

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