View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by NASA Technical Reports Server

ERDA/NASA 1002/77/10
NASA TM X-73669

FACTORS AFFECTING THE OPEN-CIRCUIT VOLTAGE AND ELECTRODE KINETICS OF SOME IRON/TITANIUM REDOX FLOW CELLS

Margaret A. Reid and Randall F. Gahn
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

(NASA-TM-X-73669) FACTORS AFFECTING THE OPEN-CIRCUIT VOLTAGE AND ELECTRODE KINETICS OF SOME IRON/TITANIUM REDOX FLOW CELLS (NASA) 17 p HC A02/MF A01 CSCL 10C

N77-26612

G3/44 Unclas 31863

Work performed for
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Office of the Assistant Administrator for Conservation
Division of Energy Storage Systems
Under Interagency Agreement E(49-28)-1002

Technical Paper to be presented at the
Symposium on Electrode Materials and Processes for Energy Conversion and Storage
sponsored by The Electrochemical Society, Inc.
Philadelphia, Pennsylvania, May 8-13, 1977

FACTORS AFFECTING THE OPEN-CIRCUIT VOLTAGE AND ELECTRODE KINETICS OF SOME IRON/TITANIUM REDOX FLOW CELLS[†]

Margaret A. Reid and Randall F. Gahn

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

E-9193

ABSTRACT

Performance of the iron-titanium redox flow cell was studied as a function of acid concentration. Anion permeable membranes separated the compartments. Electrodes were graphite cloth. Current densities ranged up to 25 mA/cm^2. Open-circuit and load voltages decreased as the acidity was increased on the iron side as predicted. On the titanium side, open-circuit voltages decreased as the acidity was increased in agreement with theory, but load voltages increased due to decreased polarization with increasing acidity. High acidity on the titanium side coupled with low acidity on the iron side gives the best load voltage, but such cells show voltage losses as they are repeatedly cycled. Analyses show that the bulk of the voltage losses are due to diffusion of acid through the membrane. No membrane tested so far will maintain differences in acidity. Chelating agents show some promise in reducing polarization at the Ti electrode and thus improving energy efficiency.

INTRODUCTION

One method that has been proposed for bulk storage of electrical energy involves the use of electrically rechargeable redox flow cells wherein all the reactive species are soluble ions (Ref. 1). A solution of electrolyte containing an oxidizing agent, Fe^{+3} for example, would pass through one side of an electrochemical cell where a portion of the ions would be reduced at the cathode. A solution of electrolyte containing a reducing agent, Ti^{+3} for example, would pass through the other side of the cell where some of the ions would be oxidized at the anode. The reactions at the electrodes would be $Fe^{+3} + e^- = Fe^{+2}$ and

[†]Work supported by Energy Research and Development Administration under interagency agreement with the National Aeronautics and Space Administration #E(49-28)1002.

STAR category 44
ERDA category UC-94c

$Ti^{+3} + H_2O = TiO^{+2} + 2\ H^+ + e^-$ for the example cited. The two electrolyte chambers would be separated by a membrane which would prevent or minimize cross-diffusion of the reactive species but allow ready transport of indifferent ions for charge balance. After passing through the cell, the partially spent fluid would be returned to the storage tank. A schematic diagram of a cell using this concept is shown in Fig. 1. Since the solutions are gradually depleted of the reactive ions, the voltage provided by the cell at a given current would gradually fall. Energy would be withdrawn from the cell at periods of high usage, and the cell would be recharged during periods of low energy demand.

This type of system could take advantage of high efficiency redox couples using high surface electrodes and not requiring expensive catalysts. Other advantages are: favorable environmental impact compared to pumped hydroelectric storage and auxiliary fuel-powered generators, immediate response to demand, ability to be located in favorable locations so as to minimize transmission losses, and the possibility of using inexpensive and readily available reactants. Disadvantages include the fact that the voltage obtainable from each individual cell is low since the reactants must be stable in aqueous solution; thus oxidation or reduction couples that react with water to an appreciable extent cannot be used. Electrical coupling of cells in series can theoretically be used to provide any required voltage, but this is limited in practice because of shunt currents if the cells are connected to a manifold. Since we are dealing with reactive materials in solution, larger volumes of reactants are needed than when the reactants are solids, and thus the sizes of storage tanks and equipment needed becomes important. At present, the estimated cost of such a system is greater than that for a pumped hydroelectric facility or auxiliary generators, and improvements in technology are required to make such a system economical in the future. The economic factors are discussed in recent publications (Ref. 2 and data obtained from G. Cyprios of Exxon Research and Engineering Co.).

Since redox flow cells are a relatively new concept in electrochemical storage, a great deal of research and development needs to be done before this type of system can become a practical reality. Studies have been made of the physical properties of possible redox solutions such as solubilities, viscosities, densities, conductivities, and solution stability (Ref. 3). Screening of possible redox couples, studies of the electrode kinetics of the most favorable ones, and investigation of possible new electrode materials is being done both at NASA Lewis Research Center (LeRC) and on contract (Ref. 3). Likewise, development and evaluation of new ion-selective membranes has been carried out both in-house at LeRC and by contract (Ref. 4). Small-scale cells have been studied extensively.

Finally, the possibility of coupling redox cells with solar cells so as to store energy in redox cells for use when the sun is not shining has been studied (Ref. 5).

This paper presents some of the results of the LeRC studies with small-scale cells. Theoretical and experimental open-circuit voltages were examined. Working voltage and current in operating cells were studied as functions of time and depth of discharge and correlated with changes in concentrations of the redox solutions, voltage losses due to polarization at the electrodes, and IR losses across the membranes.

The emphasis in this report is on cell behavior in the first few cycles, rather than the long-term behavior. Cell performance in the first few cycles is dependent more on the thermodynamics and kinetics of the system than on the particular membrane used. Long-term behavior is, however, greatly dependent on the nature of the membranes.

EXPERIMENTAL METHODS

All studies reported here were carried out using the Fe^{+2}/Fe^{+3} couple in the cathode compartment and the Ti^{+3}/Ti^{+4} couple in the anode compartment. These couples satisfied the criteria of high solubility and conductivity of all species in aqueous solution, stability in aqueous solution, and low cost. Preliminary studies indicated that the electrochemical kinetics of the Fe^{+2}/Fe^{+3} couple were satisfactory. The Ti^{+3}/Ti^{+4} couple, while less satisfactory than the Fe^{+2}/Fe^{+3} couple, behaved sufficiently well to warrant further study and use in membrane screening and systems studies. These species, in particular the Ti^{+4} ion (written as Ti^{+4} for simplicity although it probably exists as TiO^{+2} or $Ti(OH)_2^{+2}$), will hydrolyze and form oxide or hydroxide precipitates unless the solution is kept acidic (Ref. 6). All of the work reported here was carried out in HCl solution of 0.5 M concentration or greater.

Materials and equipment

Cells were tested starting with solutions in the charged state; e.g., Fe^{+3} and Ti^{+3}. $FeCl_3$ solutions were prepared from reagent grade $FeCl_3.6\ H_2O$ and HCl. $TiCl_3$ solutions were prepared by reacting technical grade Ti metal (1% Fe) in concentrated HCl and diluting to the desired concentration.

The cell design is shown in Fig. 2. The cell body is made of polycarbonate plastic. Woven, graphitized cloth 32 mils thick (0.081 cm) (Union Carbide WCA graphite cloth) was used for electrodes in both the anode and cathode compartments. Graphite tape 15 mils thick (0.038 cm) (Union Carbide Grafoil) was used for the current collector and leads from the cell. The area of membrane exposed to each solution was 2.25 in^2 (14.5 cm^2 or 1.5 in × 1.5 in). The volume of each compartment was about 2.05 cc. When the graphite electrode was in place, 1.90 cc of solution were required to fill each compartment.

For experiments with reference electrodes, 5 mm square platinum

screen electrodes were placed on both sides of the membrane and separated from the working electrodes by non-woven polyolefin fabric. A thicker gasket (about 90 mils or 0.225 cm) was needed to prevent leaks around the leads to the reference electrodes. The cell volume and electrode separation were slightly greater because of the thickness of the reference electrodes and spacers.

Most of the membranes used in this work were specially prepared for this study and were designed to be permeable to anions by incorporating amine groups (Ref. 4). An anion-selective membrane is more desirable in a cell of this type when the reactant species are positive ions since it will reduce the cross-over of reactants and thus prolong the life of the cell. In addition, in acid solutions such as these, an anion-selective membrane will reduce the transfer of hydrogen ions and decrease the possibility of hydrolysis reactions occurring if the acidity falls too low. Resistances of the membranes were measured by measuring the cell resistance with a 1000-cycle bridge and subtracting the resistance of the cell without a membrane. These ranged from about 0.1 to 0.5 ohm (volume resistivities of about 25 to 100 Ω-cm).

Experimental cycling procedure

Depending on the capacity desired, 10 to 40 ml of 1 M stock solutions were used. This represents about 0.25 to 1.0 Ah. The solutions flowed through the cells at a rate of 10 to 20 cm^3/min. Solutions draining from the cells were returned to reservoirs above the cells by a positive displacement pump or nitrogen gas-lift pump. In some experiments cells were partially discharged at constant current using a DC power supply. In most experiments they were discharged completely through a constant resistive load, usually around 1.2 ohm. The solutions were recharged using a DC power supply set at 1.2 V so as not to evolve H_2 or Cl_2. The current passed through a current integrator as well as through the cell. Completion of the charging or discharging reaction was evidenced when the current tapered off to zero.

ANALYTICAL METHODS

Determination of Fe and Cl

One-ml samples were withdrawn from the reservoirs at various points in the cycle, diluted to about 50 cc, and titrated potentiometrically with 0.025 N solutions of $KMnO_4$ or $Ce(SO_4)_2$. About 25 cm^3 of 6 N H_2SO_4 were added to maintain acidity. Titration to a potential of +300 mV ±5 using a platinum electrode with respect to a Ag/AgCl reference electrode gave the amount of Ti^{+3} present; further titration to a potential of +700 mV ±30 gave the amount of Fe^{+2}. Several sticks of amalgamated Zn were then added and the sample was brought to a boil. The hot solution was run through a Jones reductor containing 10-30 mesh amalgamated zinc

and titrated again in the same manner. The second titration gave the total amounts of Fe and Ti present in the sample. Ti^{+4} and Fe^{+3} were determined from the differences between the first and second titration.

Determination of chloride ion

One-ml samples withdrawn from the reservoirs were potentiometrically titrated with 0.2 M $AgNO_3$ to a potential of +315 mV using a silver electrode against a Ag/AgCl reference electrode with a Na_2SO_4 salt bridge. Acidity was maintained by adding 5 ml of 6 N HNO_3.

Determination of hydrogen ion

Hydrogen ion concentration was determined by difference using the relation; equivalents hydrogen ion = equivalents chloride ion - equivalents metal ions.

RESULTS AND DISCUSSION

Open-circuit and load voltages for newly prepared cells

The half-cell reactions in these cells upon discharge are $Fe^{+3} + e^- = Fe^{+2}$ and $Ti^{+3} + H_2O = TiO^{+2} + 2\ H^+ + e^-$.

An estimated equilibrium potential (or open-circuit voltage) for the Fe/Ti cell using concentrations for activities as a function of depth of discharge (DOD) is shown as curve A in Fig. 3. This curve is calculated for unit activity of hydrogen ion on the titanium side from the standard half-cell potentials (Ref. 7) using the Nernst equation to correct for changes in concentration as the cell is discharged.

Since hydrogen ion is a product of the reaction, we would expect that an increase in acidity on the titanium side would lower the theoretical open-circuit voltage. Similar curves for initial concentrations of 3 M and 6 M HCl on the titanium side are shown in curves B and C using an activity coefficient of 1.32 for 3 M HCl and 3.22 for 6 M HCl (Ref. 8). The effect of the increase in acidity as TiO^{+2} is formed also appears in these curves.

An increase in acidity should also affect the potential of the cell if the additional ions form stronger complexes with Fe^{+2} than Fe^{+3} or the reverse. The following reactions were considered;

For Fe(III): $Fe^{+3} + Cl^- = FeCl^{+2}$

$FeCl^{+2} + Cl^- = FeCl_2^{+1}$

and $FeCl_2^{+1} + Cl^- = FeCl_3$.

For Fe(II): $Fe^{+2} + Cl^{-} = FeCl^{+1}$

and $FeCl^{+1} + Cl^{-} = FeCl_2$.

Using the equilibrium constants for these reactions (Ref. 9), the concentrations of uncomplexed Fe^{+2} and Fe^{+3} ions at various depths of discharge in 0.5 M and 6 M HCl were calculated. Total iron concentration was assumed to be 1 M. The Nernst equation was used again to correct for the effect of this complex formation with the chloride ion. Curve D shows the expected open-circuit voltage for a system with 6 M HCl on the titanium side and 0.5 M HCl on the iron side, and curve E gives the expected voltage for 6 M HCl on the titanium side and 6 M HCl of the iron side. No attempts were made to calculate the effects of complexing of Ti^{+3}.

It can be seen that an increase in HCl concentration would be expected to decrease the open-circuit voltage of both the titanium and iron couples. Thus the most favorable open-circuit voltage would be obtained by using solutions with the lowest acidity needed to prevent precipitation of oxides. Since an acidity of at least 4 M is needed on the titanium side to prevent precipitation of TiO_2 within a short time, most cell cycle tests were done with 6 M HCl on the titanium side and 0.5 M HCl on the iron side. The dotted line in Fig. 3 is the experimental open-circuit voltage for such a cell. The experimental curve is higher than the voltage calculated above but agrees well with that calculated from the standard potentials given by Lingane (Ref. 7) for the titanium couple in 6 M HCl and the iron couple in 1 M HCl. Due to the fact that activities of all species are not known accurately in these solutions, close agreement with the experimental curve was not necessarily expected, but the calculations give some idea of the trends and magnitudes of the voltage changes expected.

The experimental open-circuit voltages (subsequently referred to as OCV) at 10% DOD for solutions of different acidities on the two sides of the cell are shown in the top two curves in Fig. 4. The OCVs fall with increasing acidity on both sides as predicted from the above calculations.

The load voltages at 10% DOD under a constant load of 100 mA are also shown in Fig. 4. We see that the load voltage decreases as the HCl concentration on the iron side is increased, in similar fashion to the OCV, but the load voltage <u>increases</u> as the HCl concentration on the titanium side is increased, in opposition to the behavior of the OCV. This indicates that significant polarization is taking place on the titanium side which decreases with acidity. This is also indicated by the length of time required for OCV equilibration when the HCl concentration is varied on the titanium side as shown in Fig. 5. The higher the acidity, the quicker the OCV comes to its equilibrium value, again indicating that the polarization on the titanium side decreases with increasing acidity. Similar experiments with varying acidities on the iron side

showed no differences in equilibration time, indicating that the equilibration on the iron side is much more rapid than on the titanium side. Studies with an iron concentration cell with different concentrations of Fe^{+2} and Fe^{+3} showed that equilibrium was established within 1-2 minutes.

Polarization studies with reference electrodes

The behavior of the load voltage and the delays of the OCV in coming to equilibrium as described above indicate that the major source of polarization is the titanium electrode. In order to investigate this further, several experiments were made using reference electrodes in the cell. Potential measurements were made between the working and reference electrodes and between the two reference electrodes. IR drop was measured with an interrupter technique (Ref. 10). A magnetically actuated relay with mercury-wetted contacts was placed directly in the circuit. The IR drop was determined as the nearly vertical portion of an oscilloscope trace. Some typical data are given in Table 1.

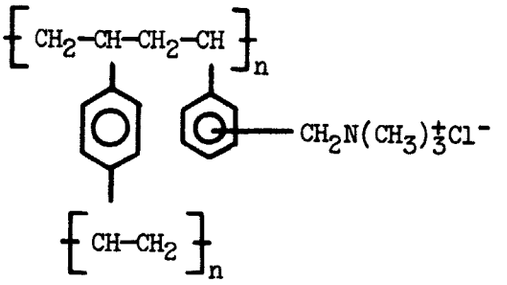
These experiments were not undertaken to provide precision data but to give the order of magnitude of the polarization and resistances in the cell.

These and similar data indicated that polarization at the titanium electrode under these conditions (6 M HCl on the titanium side and 0.5 M HCl on the iron side) amounts to over 300 mV compared to polarization at the iron electrode of 40-75 mV and an IR drop across the membrane of 30-50 mV. Several chelating agents were added to try to reduce the polarization. The most effective of these was acetylacetone. In one case the addition of 10 cc of acetylacetone to 40 cc of electrolyte on the titanium side caused a drop in polarization and a corresponding rise in cell voltage of over 300 mV.

Loss of voltage with successive cycles

One problem encountered in this work was the fact that voltages obtained on the first cycle were higher than those obtained in following cycles. The voltage fell with each successive cycle with the greatest loss between the first two cyles and smaller losses with each successive cycle. Figure 6 illustrates this effect. Detailed analyses of the two solutions during some typical runs were made to determine how much of this voltage loss was due to air oxidation of reduced species, diffusion of acid through the membranes, and diffusion of metal ions; or whether this loss of voltage was related to some effect in the membrane due to differing acidities or fouling of either the membrane or electrodes.

Table 2 presents the results of one set of analyses. The membrane used in this run was a divinyl benzene, vinyl benzene copolymer post-aminated with trimethyl amine and is typical of those used in these experiments.



Membrane QZL-B2

Metal and chloride ions were determined potentiometrically as described earlier. Hydrogen ion is determined by charge balance. The most accurate analysis is that for chloride. Attempts to obtain an accurate charge balance are hindered by the fact that slight volume changes due to evaporation through the sides of the cell, seepage, and solvent transfer are difficult to assess accurately with the present apparatus. In some cases accurate analysis of the metal ions is difficult due to the fact that the first end point in titration of solutions containing both iron and titanium is not sharp. Work is continuing on improving analytical methods.

Examining Table 2, which represents a typical case, we see that the hydrogen and chloride concentrations on the two sides of the membrane tend to equalize as the solutions are circulated even when no current is flowing. Thus, HCl is diffusing readily across the membrane from the titanium side to the iron side so that the acidity is equalized at about 3 M in a week or less. The changes in concentration of Ti^{+3} and Ti^{+4} when the initial solutions are circulated show that air oxidation of Ti^{+3} is significant. Similarly, the changes in concentration of the iron solutions in the discharged condition indicate that air oxidation of Fe^{+2} is small.

If we look at the analytical data before and after the first charge, after the HCl concentrations have approximately equalized, we can estimate the fraction of current carried by the hydrogen and chloride ions. If the chloride ion carries all the current, the hydrogen concentrations would remain the same in the two compartments and the chloride concentration would increase in the iron compartment and decrease in the titanium compartment. If the hydrogen ion carries all the current, the chloride concentration would stay the same and the hydrogen ion would decrease on the iron side and increase on the titanium side.

The analyses show that both the hydrogen and chloride concentrations change. The hydrogen concentration change is larger than that of the chloride, indicating that the hydrogen ion carries a larger fraction of the current. This is true for all membranes studied to date.

Air oxidation of Ti^{+3} will produce loss of capacity as discussed below. In addition, since there will be a greater amount of TiO^{+2} present (one of the products of the cell reaction) the voltage will be lowered. If the solutions used to fill the cell initially contain much TiO^{+2}, the initial voltages will be less than expected, and further oxidation will produce additional losses in voltage. Using the Nernst equation, we calculate lowering of voltage of 37 mV at 10% DOD for a cell in which 25% of the Ti^{+3} has been oxidized. Thus, air oxidation can account for some of the voltage losses with cycling, but not for all. Most of the initial losses are attributed to equilization in acidity on the two sides of the membrane; losses after the first few cycles are due to air oxidation of the titanium and cross-mixing of the ions. Referring to Fig. 4, we see that the change from 0.5 M HCl on the Fe side and 6 M on the Ti side to acidities of 3 M or 4 M on both sides reduces the load voltage by about 175 mV at 10% DOD. In the case depicted in Fig. 6, we have a reduction in voltage of about 75 mV at 10% DOD between the first and fifth cycle by which time the acidities should be approximately equal. The differences are believed due to the differences in discharge conditions between constant current of 100 mA (Fig. 4) and constant load resistance of 1.2 Ω (Fig. 6). The fifth cycle of Fig. 6 shows about 100 mA current at 10% DOD whereas the first cycle shows 170 mA. Qualitatively, the bulk of the loss with cycling can be attributed to equilibration of acid concentration.

Energy efficiency and current efficiency

Because of the IR drops across the membrane and solution as well as polarization losses at the electrodes, energy efficiency (i.e., watt-hr efficiency) for the Fe/Ti system is poor, at most about 40%. This is illustrated in Fig. 7, where the voltage upon charge and discharge for a typical run is plotted as a function of depth of discharge. Instead of expressing the state of charge in terms of depth of discharge, one could equally well express this in terms of the number of coulombs of charge accepted by or withdrawn from the cell. The area under the discharge curve would then be the energy obtainable from the cell in units of volt-coulombs (volts × amps × time, or energy). Likewise the area under the charging curve would be the energy required to recharge the cell. The ratio of the two areas, then, is the energy efficiency of the cell under the specified conditions of charge and discharge.

Much effort is being expended to reduce the losses in energy due to cell resistance. Membranes containing quaternary amine functional groups increase in resistance by a factor of at least two in long-term testing, whereas membranes with tertiary amine functional groups tend to exhibit better resistance stability. Some of the newer membranes show improvements in the initial resistance and long-term resistance stability and in resistance to cross-over of the metal ions.

Current efficiency (i.e., amp-hr efficiency) from one cycle to

another is close to 100% when corrections are made for air oxidation and losses due to diffusion of metal ions across the membranes. Thus only a negligible amount of current is used by side reactions such as generation of hydrogen or chlorine. However, capacity of the cells falls gradually due to cross-mixing of the metal ions and air oxidation of the Fe^{+2} produced on discharge and of the Ti^{+3} produced on charge. Table 3 shows a hypothetical example of the effects of air oxidation exaggerated for purposes of illustration. Suppose that we have a cell that initially contains 1 mole each of Ti^{+3} and Fe^{+3} (26.8 amp-hr capacity), but 0.1 mole of the Ti^{+3} is oxidized by air before the first discharge, leaving only 0.9 mole of Ti^{+3} to react with Fe^{+3}. When the cell is discharged, then, only 0.9 mole of Fe^{+2} will be produced. If further air oxidation oxidizes 0.1 mole of Fe^{+2} before charging takes place, only 0.8 mole of reduced species are available for the cell reaction, so that at the end of the first cycle, the capacity is only 80% of the original. The extent of air oxidation can be minimized by improved cell design, but some oxidation will probably always take place. Analyses of the solutions have helped to determine to what extent the losses in capacity are due to air oxidation and how much is due to metal ion cross-over. Losses in capacity due to oxidation can in principle by overcome by slight overcharging, reducing the Ti^{+4} completely to Ti^{+3} while Cl^- is oxidized to Cl_2 at the cathode. Attempts at overcharging have produced degradation of the electrode current collectors. Work is continuing on this problem.

CONCLUSIONS

Best load performance in iron-titanium redox flow cells was obtained by using a high concentration of HCl on the Ti side coupled with a low concentration of HCl on the Fe side. The open-circuit voltage decreases as acidity is increased on both the Fe and Ti sides. The load voltage also decreases when the acidity is increased on the iron side but increases with increasing acidity on the titanium side. Cells using 6 M HCl on the Ti side and 0.5 M HCl on the Fe side show voltage losses during the first few cycles. Analyses show that these losses are due to equilization of the acid concentrations on the two sides of the cell. No membrane tested to date has been able to appreciably reduce this HCl transport. Analyses have also shown that the membranes studied so far, although designed to be anion-selective, allow about twice as much transport of hydrogen ion as chloride ion during charge and discharge. Analyses of the solutions also allowed us to determine the extent of loss of capacity due to air oxidation as distinguished from losses due to mixing of the metal ions.

The increase in load voltage and the decrease in the time required for the cell voltage to reach equilibrium with increasing acid concentration on the titanium side suggests that the major cause of loss of voltage with load is due to polarization at the titanium electrode. This was confirmed by measurements of polarization with reference electrodes

which indicate that 80-90% of the polarization is at the titanium electrode. Preliminary experiments with chelating agents showed some success in reducing this polarization, notably with acetylacetone.

REFERENCES

1. L. H. Thaller, NASA TM X-71540 (1974).

2. M. Warshay and L. O. Wright, J. Electrochem. Soc., 124 (2), 173 (1977).

3. J. Giner, L. Swette, and K. Cahill, Giner, Inc., Waltham, Mass. (1976); also NASA CR-134705.

4. S. S. Alexander, R. R. Geoffrey, and R. B. Hodgdon, Ionics, Inc., Watertown, Mass. (1975); also NASA CR-134931.

5. P. O'Donnell, R. F. Gahn, and W. Pfeiffer, NASA TM X-73562 (1976).

6. C. F. Baes, Jr. and R. E. Mesmer, "The Hydrolyses of Cations," John Wiley & Sons, Inc., New York (1976).

7. J. J. Lingane, "Electroanalytical Chemistry," 2nd ed., Wiley-Interscience, New York (1958).

8. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions: The Measurement and Interpretations of Conductance, Chemical Potential and Diffusion in Solutions of Simple Electrolytes," 2nd ed., Butterworths, London (1959).

9. L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964).

10. J. Kuta and E. Yeager, "Overpotential Measurements," Techniques of Electrochemistry, E. Yeager and A. J. Salkind, Editors, pp. 177-178, Wiley-Interscience, New York (1972).

TABLE 1. - POTENTIALS BETWEEN VARIOUS ELECTRODES IN mV

Conditions	$Fe_{working} - Fe_{ref}$	$Fe_{ref} - Ti_{ref}$	$Ti_{ref} - Ti_{working}$	Cell voltage
Discharge cycle 30% DOD 150 mA load	-43	468	-311	114
Charge cycle 30% DOD 128 mA load	74	616	314	1004
IR drop by interrupter method Charge cycle Almost fully charged 103 mA current	9	32	7	49

TABLE 2. - TYPICAL ANALYSES OF REDOX SOLUTIONS AT DIFFERENT STAGES IN CYCLING. ALL CONCENTRATIONS IN MOLARITIES

	Iron side					Titanium side				
	Fe^{+2}	Fe^{+3}	Ti^{+4}	Cl^-	H^{+*}	Ti^{+3}	Ti^{+4}	Fe^{+2}	Cl^-	H^{+*}
Initial solutions	----	1.00	----	3.50	0.50	0.87	0.08	----	7.46	4.54
Circulated one day, no current flow	0.01	0.99	0.08	4.29	1.00	0.79	0.15	0.03	7.23	4.19
First discharge, one day later	0.85	0.09	0.09	4.87	2.54	0.02	0.93	----	6.25	2.45
Circulated one day after discharge, no current flow	0.87	0.04	0.08	5.44	3.29	0.02	0.89	----	5.95	2.34
First charge, one day later	----	0.93	0.05	5.72	2.76	0.73	0.16	0.01	5.66	2.82

*Hydrogen ion concentrations are calculated from charge balance on the basis that Ti(IV) is present as Ti^{+4}. This eliminates the change in hydrogen ion concentration resulting from the reaction ($Ti^{+4} + H_2O \rightleftarrows TiO^{+2} + 2H^+$) and therefore measures the transference across the membrane. Actual hydrogen ion concentration is probably higher by an amount equal to twice the Ti^{+4} concentration.

0193

TABLE 3. - EFFECT OF AIR OXIDATION ON CELL CAPACITY

	Fe^{+3}	Fe^{+2}	Ti^{+3}	Ti^{+4}	Charge delivered (accepted) (Faradays)
Moles in original solutions	1.0	0.0	1.0	0.0	---
Moles after oxidation by air before discharge	1.0	0.0	0.9	0.1	---
Moles after discharge	0.1	0.9	0.0	1.0	0.9
Moles after oxidation by air before recharge	0.2	0.8	0.0	1.0	---
Moles after charge completed	1.0	0.0	0.8	0.2	0.8

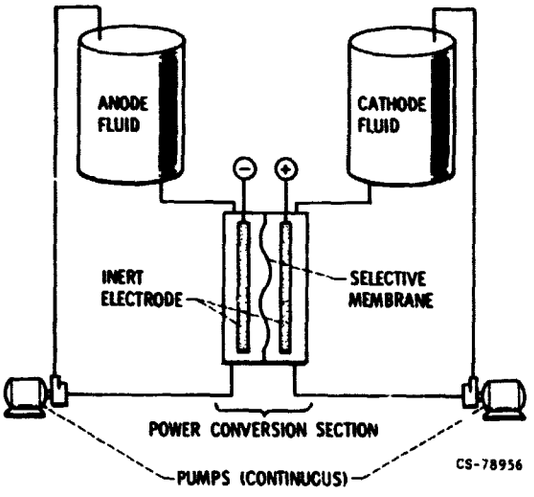


Figure 1. - REDOX system.

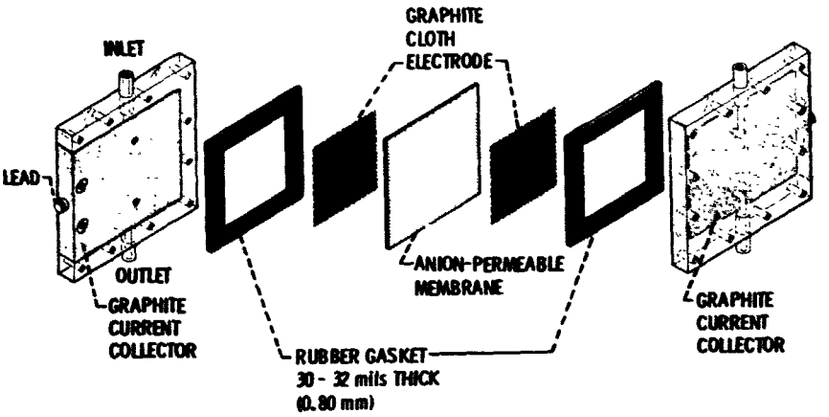


Figure 2. - Exploded view of experimental cell.

A. UNIT ACTIVITY OF H^+, NO CORRECTIONS FOR ACTIVITY COEFFICIENTS (γ) OR COMPLEX FORMATION.
B. 3 M HCl ON Ti SIDE, γ_{HCl} = 1.32, NO CORRECTIONS FOR COMPLEX FORMATION.
C. 6 M HCl OF Ti SIDE, γ_{HCl} = 3.22, NO CORRECTIONS FOR COMPLEX FORMATION.
D. 6 M HCl ON Ti SIDE, γ_{HCl} = 3.22; 0.5 M HCl ON Fe SIDE, CORRECTED FOR COMPLEX FORMATION.
E. 6 M HCl ON Ti SIDE, γ_{HCl} = 3.22; 6 M HCl ON Fe SIDE, CORRECTED FOR COMPLEX FORMATION.

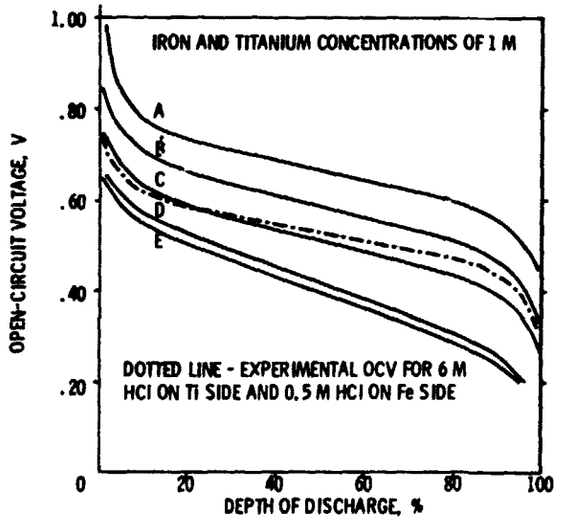


Figure 3. - Theoretical open-circuit voltages for the iron-titanium redox cell at varying acidities.

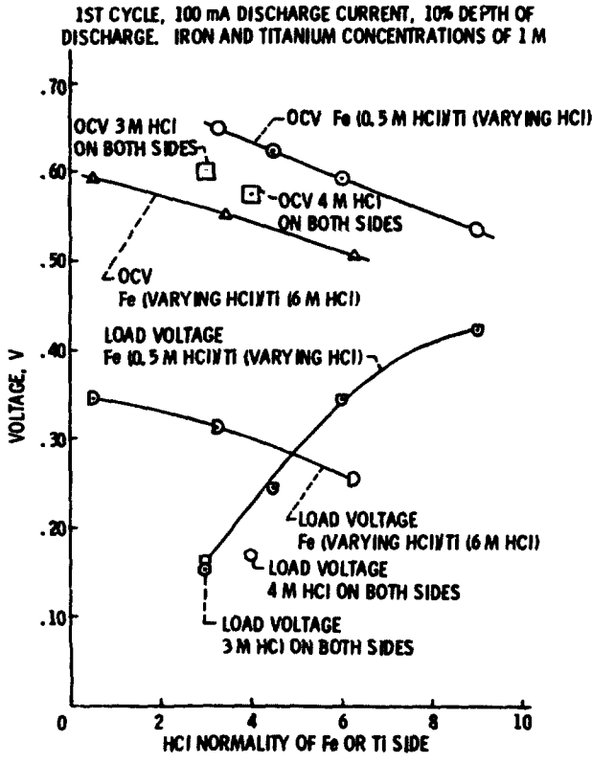


Figure 4. - Experimental open-circuit and load voltages for an iron/titanium cell.

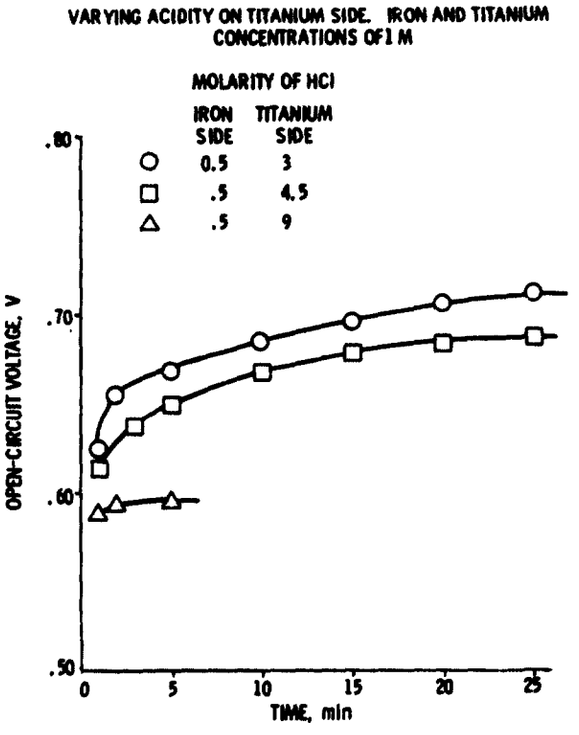


Figure 5. - Open circuit voltage equilibration following five minute discharge at 100 mA current.

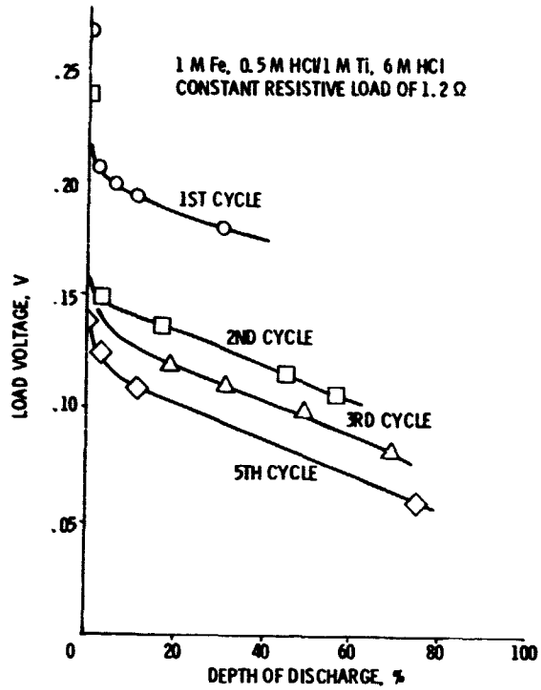


Figure 6. - Loss of load voltage as cell is cycled.

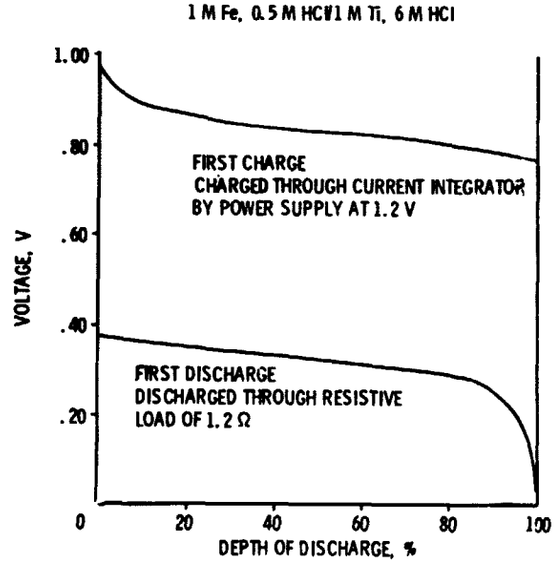


Figure 7. - Voltage on charging and discharging to obtain energy efficiency.