RECENT ADVANCES IN REDOX FLOW CELL STORAGE SYSTEMS

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Recent advances made in membrane and electrocatalyst technologies as they relate to the iron chromium Redox system have brought this energy storage concept to the point where complete systems have been designed, built and tested. Several novel features have been conceived and incorporated into complete Redox systems that greatly enhance its ability to be kept in proper charge balance, to be capable of internal voltage regulation, and in general be treated as a true multicell electrochemical system rather than an assembly of single cells that are wired together. The paper will cover the recent data pertaining to the system-related features as well as the state of the technology of the Redox membranes. The technology status as it relates to the two application areas of storage for solar photovoltaic/wind and distributed energy storage for electric utility applications will also be addressed. The cost and life advantages of Redox systems will also be covered.
ABSTRACT

Recent advances in Redox flow cell storage systems have been designed, built, and tested. Several novel features have been conceived and incorporated into complete Redox systems that greatly enhance its ability to be kept in proper charge balance, to be capable of internal voltage regulation, and in general be treated as a true multi-cell electrochemical system rather than an assembly of single cells that are wired together.

The paper will cover the recent data pertaining to the system-related features as well as the state of the technology of the Redox membranes. The technology status as it relates to the two application areas of storage for solar photovoltaic/wind and distributed energy storage for electric utility applications will also be addressed. The cost and life advantages of Redox systems will also be covered.

FIVE YEARS AGO the concept of an electrochemical storage system based on two fully soluble redox couples separated by an ion exchange membrane was presented at the 9th IECEC meeting (1*). In conceptual form, the use of tanks to store redox fluids and pumps to circulate the stored reactants through the stack of individual Redox flow cells was described. The potential advantages of this concept, in which the storage portion of the overall system can be sized independently of the power-related portion of the system and in which no solid electrode reactants are present, were outlined.

At the present time, ion exchange membranes meeting the extremely stringent selectivity and area resistivity requirements are well on their way to being fully developed. Redox couples (Fe<sup>2+</sup>/Fe<sup>3+</sup>, Cr<sup>2+</sup>/Cr<sup>3+</sup>) when used with suitably catalyzed electrode structures have been developed that possess such very high current exchanges that complete Redox cells operate reversibly out to current densities in the hundreds of amperes per square foot. The hardware used for testing membranes and electrodes has grown from single cells with an active area of 0.0156 ft² to multi-cell stacks where the active area of each cell is 0.33 ft².

Currently the ferrous/ferric redox couple and the chromous/chromic redox couple are being used as the positive and negative reactants, respectively. These solutions are one molar chlorides of the respective cations in two normal hydrochloric acid supporting electrolyte. The membranes and electrocatalysts were developed under contract by Ionics, Incorporated of Watertown, MA, and Giner, Incorporated of Waltham, MA, respectively.

The list of advantages for Redox systems has grown as the Redox technology has matured from the conceptual stage to the present status of actual working systems with predictable performance, high reliability, stable operation and long life. Applications for this technology in the near-term include energy storage for stand-alone village power systems that use solar photovoltaic or wind energy as their primary energy source. As the technology advances further, distributed energy storage installations in electric utility service will become possible. The current cost projections for this technology appear very attractive compared with lead acid batteries. Moreover, its most attractive features are related to the ease with which Redox technology may be handled at the total system level.

The near-term application for NASA-Redox energy storage systems will be small village power systems where solar arrays or wind turbines would provide the power but where storage is required for night-time or periods of low sun or wind levels. This application (2) is characterized by having small power requirements (5 to 25 kW) but where rather long durations of dependence on the storage devices is required (30 to 60 hours). This type of application is ideal for Redox systems since long storage times require only expanded reactant fluid and storage tank volumes.

The basic fluid schematic for a full-function Redox system is shown in Figure 1. It should be noted that an open circuit cell and a rebalance cell have been added to the basic Redox system described in earlier presentations. The function of the open circuit voltage cell is to provide a continuous direct reading of the state-of-charge or the depth-of-discharge of the entire Redox system. As its name implies, this cell is never placed under load but simply reads the voltage of the redox solutions that are flowing through it. The cell itself may be located hydraulically in parallel with the flow to the other cells in the stack if the state of charge of the incoming solutions is required or in series downstream of the stack if the state of charge of the exiting solutions is being monitored. The voltage of the open circuit voltage cell is approximately

\[ E = 1.075 - 0.59 \log \left( \frac{[Cr^{3+}]}{[Cr^{2+}]} \times \frac{[Fe^{2+}]}{[Fe^{3+}]} \right) \]

This voltage may be directly related to the state of charge of the system as a whole.

The function of the rebalance cell is to allow the state of charge of the negative reactants to be maintained at exactly the same state of charge as the positive reactants. This cell can correct for the cumulative effects of: (1) coevolution of hydrogen, hydrogen at the negative electrode during the charge portion of the cycle, (2) any chemical reduction of hydrogen ion by chromous ions, (3) any air intrusion into the system reactant solutions causing air oxidation of either some of the ferrous or chromous ions. It should be noted that whether the small amounts of hydrogen from within the cell are being used for rebalancing or hydrogen from an external supply is being consumed in a rebalance process, it is being performed at the system level without any need to take the actual Redox stack out of service.

The Redox stack is sized to produce the desired system output. Typically, these cells are connected in a bipolar manner with inlet and exit manifolds used to supply reactant flow to each of the cells which are connected in parallel hydraulically. The use of fully soluble reactants permits the added feature of trim cells to be employed. For instance, a fourteen cell stack may have the last three cells equipped with current leads so that either twelve, thirteen, or the full fourteen cells may be connected in series. This feature permits a type of internal voltage control while at the same time does not leave different parts of the system at different states of charge.

*Numbers in parentheses designate References at end of paper.
When all of these features are combined in a stack, the configuration shown in Figure 2 results. These full-function stacks have been built and tested to verify and satisfactorily demonstrate all the above mentioned features. In addition, stack performance, in terms of power output and efficiency, clearly demonstrates the potential of Redox for development into inexpensive, highly versatile energy storage systems.

The technology program that has been carried out with a combination of funding from the Department of Energy and the National Aeronautics and Space Administration consists of the following elements.

1. Ion exchange membranes
2. Inert electrodes
3. Flow cells
4. Small cell stacks
5. System cost and performance projections

Each of these elements will be reviewed in terms of the progress to date compared with goals established on the basis of anticipated system requirements.

1. ION EXCHANGE MEMBRANES

In Redox cells, the membranes separating (Fig. 1 and 2) the iron and chromium solution must be highly selective with respect to these ions and yet permit the free passage of chloride ions. These membranes are described as fabric supported, crosslinked polyelectrolyte, ion exchange membranes. Although they operate in highly concentrated solutions where the simple Donnan Exclusion Principle is no longer valid, the principle of having the highest concentration of ion exchange groups possible in conjunction with a very carefully engineered pore structure has been followed in the membrane development efforts. The contractor has been Ionics, Inc., of Watertown, MA (§ 6). Typically, these membranes are made by mixing the two portions of the desired polymer (backbone and crosslinker) in the desired proportion along with the desired fraction of a non-polymerizable material. This mixture is then poured over a fabric which imparts a degree of strength to the finished membrane. This wetted fabric is placed between two linked agent, the fraction and type of nonpolymerizable material. The resultant material is then soaked in water. This is the form of the membrane material that is used in Redox cell tests. The membranes are characterized for area resistivity, selectivity to iron ion and chromium ion crossover, ion exchange capacity, and thickness. The membranes investigated have covered different monomers, the ratio of backbone to crosslinking agent, the fraction and type of nonpolymerizable content of the initial mixture, and fabric type and thickness. Table 1 is a brief summary of the best results over the past few years.

Table 1 - Summary of Anion Exchange Membrane Characteristics

<table>
<thead>
<tr>
<th>Membrane Designation</th>
<th>Year</th>
<th>Selectivity (µg/hr/cm²/M/L)</th>
<th>Area Resistivity (Ω-cm² in 1N HCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10ZQZL-219 (Standard)</td>
<td>1974</td>
<td>150</td>
<td>1.7</td>
</tr>
<tr>
<td>A4L-28A</td>
<td>1976</td>
<td>110</td>
<td>1.3</td>
</tr>
<tr>
<td>A3L-87P</td>
<td>1977</td>
<td>14</td>
<td>2.8</td>
</tr>
<tr>
<td>CD1L-45</td>
<td>1978</td>
<td>10</td>
<td>2.0</td>
</tr>
</tbody>
</table>

It can be seen that significant progress has been made in making highly selective membranes. It has been found that the area resistivity of these membranes increases when exposed to the actual Redox cell environment with certain formulations being more sensitive to this than others. The 2.0 Ω-cm² resistivity will typically increase to about 5 Ω-cm² in a "well-behaved" membrane. The phenomenon has been traced to an interaction of the membrane with the ferric ion.

The goals that have been set for membrane properties are different for the solar photovoltaic and the electric utility application. This stems from a difference in the ratio of power to storage duration of these two applications, plus certain assumptions relating to performance requirements. The goal for the solar photovoltaic system application based on anticipated performance requirements is an area resistivity in a Redox environment of 3.3 Ω-cm² and a selectivity of about 25 µg of crossover/hr/cm²/N/L. This selectivity would typically result in only a 25% loss of capacity after 20 years. For the electric utility storage applications where higher current densities and shorter storage times are envisioned, the respective goals are more stringent; 1.5 Ω-cm² and a selectivity of 5 µg crossover/hr/cm²/N/L. Currently, the area resistivity (Table 1) is more of a problem than the selectivity.

2. INERT ELECTRODES

There are, of course, no plating or deplating reactions with Redox cells. The electrodes serve only as current collectors and reaction sites for the redox reactions. Carbon and graphite felts and cloths have received prime consideration for this application (§ 6). All the materials that were tried produced poor results. Under contract, Giner, Inc., Waltham, MA (7) succeeded in defining a gold-lead catalytic system for the chromium reactions. Small amounts of gold are plated into an inert substrate thus lead acts as a gold electrode. During charge, the lead deplates and the electrode acts as a gold electrode. Gold has been found to render the oxidation of chromous ion reversible. Typical results obtained by Giner on non-porous rotating graphite electrodes are shown in Figure 3. Data for the uncatalyzed carbon surface is shown for comparison. When this catalyst system was adapted in our laboratory to porous carbon and graphite felts, greatly improved cell performance resulted. Figure 4 shows the progression of improvements in performance of laboratory sized cells (14.5 cm²) that were run with a highly conductive membrane formulation. Over the time span of a year, the peak power from these cells increased from about 10 watts/ft² to about 95 watts/ft².

Because of the voltage swings experienced by the chromium electrode between full charge and full discharge (+.5 to +.3V vs. SHE), the lead (%100 µgm/cm²) can be expected to undergo plating and deplating during each cycle. Cycling tests conducted in complete Redox cells have been carried out on several electrode constructions to test for performance decay. The Redox cells used for this purpose have very small fluid inventories so that as many as forty complete cycles per day may be carried out. Every 500 cycles the electrodes are subjected to a series of standard charge and discharge current densities to determine if any electrode deterioration has taken place.

To date no deterioration after 3000 deep discharge cycles has been demonstrated. This, of course, would meet or surpass any goal for an electrode used for solar applications. These electrodes are also fully reversible and free from mass transfer effects out to several hundred amps/ft² under proper flow conditions.
3. FLOW CELLS

In any type of electrochemical system based on flowing the reactants through a porous electrode structure, there are a number of tradeoffs. These are associated with shunt currents, pumping power, cell performance and reactant inventory. At very low flow rates, the condition may be reached where the reactants in the solutions are fully depleted just as they leave the cell. This is referred to as the stoichiometric flow rate. At these flow rates, a very large change in the Nernstian correction (log (Fe^3+)/Cr^3+)/(Fe^+/Cr^2+) x (Fe^+/CFe^+)/(Fe^3+)) takes place with its associated reduction in cell voltage. Even at flow rates above stoichiometric, poor performance may result if diffusion limiting currents are approached. On the other hand, high flow rates are associated with some compromise in pumping power and high shunt current losses. Some of the information required to assess these various ramifications can be obtained from a performance map of a single flow cell. Figure 5 shows the cell performance map of a single flow cell. Figure 5 shows the cell performance of one cell of a five cell stack operated at steady state conditions at various current densities and flow rates. At high flow rates, the separation of the lines is a function of the internal resistance of the cell. At the lower flow rates, Nernstian corrections also must be considered. The stoichiometric flow rate at each current density for the condition of the test (50% DOD) is noted on the plot. The cell used in these studies was the standard 0.33 ft^2 cell. In this cell configuration (Fig. 2) a narrow inlet and outlet slits connect the main manifold to the secondary manifolds at the base of the electrodes. The secondary manifold allows the incoming liquid to spread out along the width of the electrode prior to its flow through the carbon felt electrode placed in the cavity between the membranes and the bipolar plate. This sheet flow proceeds from the bottom of the cell up to the top where another manifold connects to the each of the exit manifolds from the electrodes. Considering pumping requirements, Figure 6 gives the relationship between pressure drop and flow rate. Superimposed on the plate are the dimensions and plan form of the cell used. At several points the actual ideal pump powers are noted. This cell when operated at 50 amps/ft^2 delivers about 15 watts. The pumping requirements represent a minor efficiency penalty.

4. SMALL STACKS

Advances in membranes, electrodes and flow field design all come together at the small stack level of testing. This work was started in the spring of 1978, with what were called iron/iron cells. These five-cell stacks of 0.33 ft^2 cells were operated with ferrous/ferric solutions at both electrodes. Since this redox couple is fully reversible without the need for any catalyst, these cells were used to explore mass transport effects caused by variations in flow rate and flow field configuration. It was from this type of testing that the selection of sheet flow was made. As techniques were developed to produce large scale gold-lead catalyzed carbon felt electrodes, five-cell iron/chromium Redox stacks were tested. Table 2 lists some experimental data gathered from development stack No. 7.

Table 2 - Summary of Data-Stack No. 7

| Number of Cells | 5 (.33 ft^2 active area) |
| Flow Type | Sheet |
| Fe-Electrode | .125" Carbon Felt |
| Cr-Electrode | .125" Carbon Felt, Au-Pb catalyzed |
| Cell Resistivity | .0050 Q-Ft |
| Membrane Resistivity | .0026 R-Ft (in 1N HCl) |
| V (discharge)/V (charge) | .86 , .82 , .70 |
| at 10,20,30 asf at 50% DOD | 70 |
| Stack Power | 50 watt/ft^2 at 75 amps/ft^2 |
| Charge/Discharge Cycles | 70 |
| Amp-hr efficiency | 96-99% |
| (Goal-95%)* watt-hr efficiency | 70-80% |
| (Goal-75%)* |

*At 20 amps/ft^2

The polarization curves on charge and discharge for this stack are plotted in Figure 7. The performance necessary in order for this type of hardware to meet the anticipated requirements for solar applications is 0.9 volts/cell at 50 amps/ft^2 at 50% depth of discharge. To meet this goal, a further reduction in the overall cell resistance is still required. The major part of the internal resistance still resides in the membrane.

To the basic hardware used in stack No. 7, several features were added that resulted in what is referred to as a full function Redox stack (Fig. 2).

OPEN CIRCUIT VOLTAGE CELL - The open circuit voltage of a redox half cell is given by the simple relationship:

\[ E = E^0 + \frac{RT}{nF} \ln \left( \frac{[\text{Reactant}]}{[\text{Product}]} \right) \]

For the situation in which the iron and chromium redox couples are involved in a complete cell reaction in chloride solutions (where complexes are formed) the equation

\[ E = 1.075 - .059 \log \left( \frac{[\text{Cr}^{3+}] [\text{Fe}^{2+}]}{[\text{Cr}^{2+}] [\text{Fe}^{3+}]} \right) \]

is approximately correct. The value of 1.075 is experimentally obtained from measurement of the open circuit voltage at 50% state of charge. Once \( E^0 \) is known, the state of charge of the system is related in a simple manner to the open circuit voltage.

REBALANCE CELL - In common with other battery systems, repeated cycling of Redox systems will result in the reactants becoming out of balance in terms of capacity. Because the solutions are common to all cells, the imbalance in Redox systems occurs at the system level rather than at the individual single cell level as is the case with traditional battery systems. If chromous ions were allowed to be oxidized with air, or if, during the charge cycle, hydrogen is evolved instead of chromic ions being reduced, the reactant solutions would become out of balance. If this out-of-balance condition were to be uncorrected, a permanent loss of usable system capacity would result. The rebalance cell (Fig. 1), a unique feature in Redox technology, consumes ferric ions from the circulating iron solution and hydrogen gas either from the ullage over the chromium solution or from an external hydrogen source. The reactions taking place within the rebalance cell have the net effect of returning the Redox solutions to electrochemical balance.
The major cause of imbalance in Redox systems is the coevolution of hydrogen at the chromium electrode on charge. This may account for a 2 to 5% loss in ampere hour efficiency. One rebalance cell can thus continuously balance a system having 20 to 50 Redox cells. Other reactions with minor significance that are also corrected for in this way are air intrusions into the iron solution and the slow liberation of hydrogen from the chemical reduction of hydrogen ion by chromous ion. A more detailed explanation of these reactions in the rebalance aspects of Redox technology are to be found elsewhere (8).

To illustrate, a rebalance cell was added to one of the small lab sized cells (14.5 cm² active area). Figure 8 shows the result of the internal rebalance mode of operation. The rate of loss of capacity is reduced by rebalancing most of the coevolved hydrogen gas during recharge. The further effect of external rebalance is seen in Figure 9. Here, external hydrogen is consumed in the rebalance cell to counter other loss mechanisms. It should be noted that the Redox cell in the system does not need to be withdrawn from service while the rebalance process is being carried out.

TRIM CELLS - The operating voltage of a stack of Redox cells varies over a wider span than does a battery system where the electrochemical reactants are solids in both states of charge. This is caused primarily by the rapid change in the Nernst correction at shallow and deep depths of discharge. From a voltage regulation standpoint, this condition is undesirable. However, due to the use of a common set of circulating fluid reactants, extra cells may be switched into or out of the stack circuit to adjust the output voltage to within desired limits. This practice when used in the traditional battery context is referred to as end cell switching; but the end cell(s) would not be at the same state of charge as the other cells in the battery. In a Redox system, the use of trim cells would not result in different parts of the system being at different states of charge. The output potential of the open circuit voltage cell described earlier or the stack output voltage could be used to provide the signal to automatically control this switching.

FULL-FUNCTION SYSTEMS - A full-function Redox system contains the above mentioned features. Figure 2 depicts a stack that incorporates these full-function cells. Also a blow-up of the simple repeating units within a stack are shown. All of these features have been built into and successfully tested in 0.33 ft² sized hardware. A small but complete system built for demonstration purposes is shown in Figure 10. The 100-watt average, 200-watt peak stack was used with five gallon storage tanks. These full-function systems have the following characteristics:

1. They are fully capable of all reballancing requirements being performed at the system level on a continuous basis without removal of the stack from service.
2. They can provide an accurate, continuous non-mechanical state-of-charge indication to drive any associated system control logic.
3. They can stay within any reasonable voltage tolerance band during the charge or discharge portion of the cycle.
4. Permanent capacity loss will only result from membrane degradation. Present membranes are now available that would result in only a 25 percent loss of original capacity over a 20 to 30 year period of time.

SYSTEM PROJECTIONS

The recent advances in the electrode performance and the membrane selectivity and resistivity characteristics have resulted in the ability to generate near-term system designs with a considerable degree of confidence. For a solar storage application, a performance of 45 watts/ft² and 0.9 volts per cell at 50% DOD was assumed. This sizes the stack. The tank sizes assume a greater than stoichiometric amount of reactants: a 20 percent excess is assumed to account for the cycling between 10% and 90% depth of discharge; a further 25% excess of reactants is also added to account for capacity losses over some projected system life requirement. This allows the system to be able to meet its 'nameplate' capacity after 25 to 30 years of life. For a small Redox system with 10 kW output over a 50-hour storage duration (500 kWh), the component sizes are approximately as depicted in Figure 11. The right circular cylinder tanks are about 10.75 ft, when 1 Molar solutions are used. The Redox stack itself would be about 2 ft. x 2 ft. x 4 ft. and would contain about 225 ft² of cell area. The current cell performance is about 23 watts/ft² at 0.9 volts. Further improvements in cell performance are thus required. The preliminary cost projections for these systems is $24/kWh for a 50-hour storage system. This is based on projections based on current production techniques for similar-type hardware built for water electrolysis and fuel cells. More direct and less costly production technique for chromium chloride is assumed. This production does appear to be feasible and preliminary pricing studies have already been completed. More refined hardware cost studies are currently being performed under contract by the Power System Division of United Technologies. By comparison, lead acid batteries for this type application cost about $100 per kWh and yet lack many of the system features that are inherent with Redox energy storage systems.

CONCLUDING REMARKS

Redox energy storage systems based on iron and chromium chloride solutions have been built and tested in very small sizes (100-watt, 400-watt hour). These systems have demonstrated all the attractive features that are inherent to the Redox technology. Electrode performance and cycle life results based on accelerated tests are sufficient to meet the currently perceived requirements for both the solar photovoltaic/wind and the electric utility application. The membrane selectivity is more than sufficient for solar applications but further improvements are needed for the electric utility application. Membrane area resistivity in the Redox environment is the present pacing item. Slight improvements in this area are needed for the solar application (from 5.8 Ï·cm² to 5.3 Ï·cm²) and significant improvements for the electric utility application (5.8 Ï·cm² to 1.8 Ï·cm²). These are not viewed as monumental advances in the state-of-the-art since the major factor involved in the membrane area resistivity is an interaction between the chloro complex of iron in the ferric state. Typical membrane area resistivities in hydrochloric acid solutions are 2.0 Ï·cm². The main thrust of further membrane development will be directed at reducing this interaction.

REFERENCES


FULL FUNCTION REDOX FLOW CELL SYSTEM

REVERSIBLE ELECTRODE COMPARED TO IRREVERSIBLE ELECTRODE

REDOX STACK AND SINGLE CELL COMPONENTS

REDOX STACK AND SINGLE CELL COMPONENTS

DISCHARGE PERFORMANCE OF SUBSCALE CELLS

PERFORMANCE MAP OF A 0.33 ft² CELL AT 50% DEPTH OF DISCHARGE
PRESSURE DROP VS. FLOW RATE FOR .33 m² CELL CONFIGURATION USED IN SHORT STACKS

![Pressure Drop vs. Flow Rate Graph](image)

Figure 6

CHARGE AND DISCHARGE CHARACTERISTICS OF IRON/CHROMIUM STACK NO. 7

![Charge and Discharge Characteristics Graph](image)

Figure 7

EFFECT OF REBALANCE CELL ON SYSTEM CAPACITY LOSS RATE

![Effect of Rebalance Cell on System Capacity Graph](image)

Figure 8

CAPACITY RETENTION OF A SYSTEM EQUIPPED WITH REBALANCE CELL USING BOTH INTERNAL AND EXTERNAL REBALANCE MODES

![Capacity Retention Graph](image)

Figure 9

Figure 10

Figure 11