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RECHARGEABLE REDOX FLOW CELLS (NASA)  
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### ELECTRICALLY RECHARGEABLE REDOX FLOW CELLS

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## ELECTRICALLY RECHARGEABLE REDOX FLOW CELLS

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In recent years economic factors within the electric utility industry have led to the quest for means of storing bulk quantities of electrical power. A number of methods have been put forward as possible contenders for this application: compressing and storage of air in large caves or mines, advanced flywheels, capacitive storage, inductive storage and a number of electrochemical schemes. To this date only pumped water storage has proven to be a viable method of providing the needed capability.

Considering the topographical and sizing requirements for a typical pumped water storage installation and the emergence of energy conversion schemes that are time dependent as to their generating capability (e.g., solar electric, windmill electric), a closer look is being given to nonpumped water storage schemes for storing electricity. An electrochemical bulk power storage concept, which we have named a rechargeable redox flow cell is described. This scheme, based on pumping a redox couple through a power conversion section, appears to offer high overall efficiency, no cycle life limitations for the electrodes, and deep discharge capability.

### INTRODUCTION

The field of bulk power storage has been dominated by pumped water storage. The first of these facilities was the Rocky River Pumped Storage Plant (ref. 1) in western Connecticut built in 1928 with a capacity of 32 MW. The great interest in building pumped hydro facilities in recent years stems from economic factors associated with the electric utility industries (refs. 2 and 3). There are a number of concepts that compete with pumped hydro in principle, but these are either unattractive from a cost standpoint (lead acid batteries) or have not as yet been developed to the point where a valid cost and life estimate can be made. The electrically rechargeable redox flow cell falls in this latter case.

Redox cells (soluble electrodes in both charged and discharged state) are by no means new. In general, these systems were designed to be regenerable on a continuous basis using oxygen, charcoal, radiation, etc. to supply the energy for the regeneration.

The concept presented here would use a tank of cathodic fluid (concentrated  $Fe^{+3}$  for example) a tank of anodic fluid (concentrated  $Ti^{+3}$  for example) and a power conversion section which would consist, at the single cell level, of two electrolyte chambers containing inert electrodes separated by an ion specific membrane. Pumps for the cathodic and anodic fluids would continuously circulate these fluids through their respective electrolyte chambers. If the redox couples are selected based on having a high degree of reversibility and the selectivity of the membrane would preclude the transport of the redox ions, a long life,

very efficient electrochemical system would result that could be scaled and built into systems of the size required for bulk power storage application. Systems built around this concept will probably not possess high energy densities but will have high overall electrical efficiencies.

### 1. The Concept

Rechargeable redox cells are by no means new (ref. 4). The classic examples of these systems were based on chemical recharging. Air for example was employed to reoxidize ferrous ions to the ferric state or bromide ion to elemental bromine (or  $Br_3$ ). On the anode side, hot activated carbon beds were used to reduce ferric ion to ferrous ion. The overall reaction of such systems could be thought of as:



This represents the ultimate goal of the early fuel cell workers of generating electricity directly from the combination of coal and air.

The electrically rechargeable redox flow cell on the other hand is conceived as a system for application in the bulk energy storage area where overall energy efficiency is of prime importance. Figure 1 pictorially describes the concept of the electrically rechargeable redox flow cell. Storage tank A contains a redox couple primarily in its reduced state and acts as the anode material. Storage tank B contains another redox couple but one primarily in its oxidized state and acts as the cathode material. These fluids are pumped to a power conversion section C where there are two inert electrodes separated by a suitable membrane which prevents ions from the cathode redox couple from mixing with the ions from the anode redox couple. As the fluids flow over the inert electrodes, electrochemical action can take place if an electrical load is applied to the cell. The fluids in their discharged state are collected in their respective storage tanks D and E. The system can be electrically recharged by applying a suitable voltage to the terminals of the power conversion section as the fluids are pumped from the tanks D and E back up to tanks A and B. The power that can be withdrawn from or put back into the system depends on many factors including the tank volumes, the flow rates and the electrochemical features of the redox couples and the electrode compartments.

The concept of the electrically rechargeable redox flow cell contains some similarities of the fuel cell wherein reducible and oxidizable fluids are flowed into a stack of cells where electrochemical reactions take place. The fact that the system may be recharged by simply reversing the flow of current and fluids also makes it similar to a secondary battery.

## 2. Electrode Considerations

The selection of electrode materials for an electrically rechargeable redox flow cell involves several simple criteria:

(a) Both the oxidized and reduced species must be soluble.

(b) The oxidation and reduction potentials of the different species must be such that the solvent will remain inert during charging as well as on stand.

(c) Oxygen containing or demanding ions (e.g.,  $\text{MnO}_4^-$ ,  $\text{Cr}^{+3}$ ) should be avoided to simplify hydrogen ion management problems.

(d) Complexed ions (e.g.,  $\text{Fe}(\text{CN})_6^{4-}$ ) should be avoided to minimize overall system weight.

The first criterion simply encompasses the classical type of redox electrode such as the ferrous/ferric couple in a chloride solution.



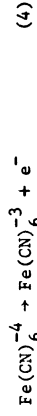
Here both the chlorides are highly soluble and the inert electrode does not become fouled or complicated by the presence of insoluble species. Charge neutrality is maintained by the diffusion into or out of the half cell compartment of some other type of ion (i.e.,  $\text{H}^+$  or  $\text{Cl}^-$ ).

The second criterion deals with the requirement of maintaining the solvent as a neutral species during charge, stand, and discharge. If water is the solvent, ions above hydrogen in the list of oxidation/reduction potentials should be avoided ( $\text{Cr}^{+2}$ ,  $\text{V}^{+2}$ ,  $\text{Tl}^{+2}$ ), since hydrogen could be displaced. On the other end of the scale ions such as  $\text{Co}^{+3}$ ,  $\text{Ce}^{+4}$ , and  $\text{Mn}^{+4}$  could possibly displace oxygen from solution. Care must also be exercised during the charging process where the overpotentials applied could lead to the simultaneous discharge of solvent fragments along with the desired ions.

Criterion three comes into consideration when the overall charge balance and ion management schemes are arranged. Consider the permanganate ion reduction.



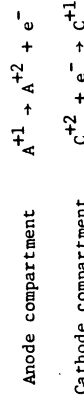
Eight hydrogen ions are required for this half cell reaction. In a complete system, large amounts of acid would be required and pH changes would be large. This may be contrasted with the ferrous/ferric half cell reaction (2) which requires no hydrogen ions. The fourth criterion is an extension of the third. The ferri/ferro cyanide couple will serve as an illustration.



Although the above pair of half cell reactions meet the first three criteria, the equivalent weight of the cyanide complex is 272 as opposed to 56 for the noncomplexed iron. Thus, from an energy density standpoint the use of complexed ions is not desirable.

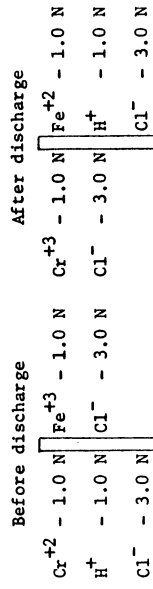
## 3. Membrane Considerations

The requirements and options in regard to the membrane that is used to separate the anode and cathode fluids can be illustrated by considering a simple redox cell system with the reactions written in the discharge direction.

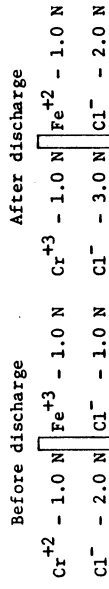


The membrane must provide an impermeable barrier to both the A and C ions in both states of charge. Further, it must provide the means by which charge neutralization is maintained. During discharge either positive ions ( $\text{H}^+$ , for example) must move from the anode compartment through the membrane to the cathode compartment or negative ions ( $\text{Cl}^-$ , for example) must move from the cathode compartment to the anode compartment. There is an inherent disadvantage from an energy standpoint in moving positive ions from the anode compartment during discharge as opposed to the other option. The iron/chromium system will be used to illustrate this. An ideal hydrogen ion transport membrane and an ideal chloride ion transport membrane will be used in the illustration.

### Case 1. - $\text{H}^+$ membrane



### Case 2. - $\text{Cl}^-$ membrane



In Case 1 as compared to Case 2, 1 mole of HCl is required per Faraday over and above any acid that may be required for pH adjustment needed for solution stabilization. In addition, an anion membrane would most likely have a better selectivity for preventing cross diffusion of the redox ions. Cross diffusion of such ions would represent a permanent loss of system capacity.

## 4. System Considerations

In the Concept section the system was depicted using four tanks. It is felt that two tanks would lead to a more efficient overall system. Figure 2 illustrates the two tank system and figure 3 depicts the voltage vs. depth of discharge relationship starting with 2.0 M  $\text{Fe}^{+3}$  and 2.0 M  $\text{Cr}^{+2}$ . For simplicity ideal solutions were assumed. If the system was designed to cycle between 5 and 95 percent depth of discharge the open circuit voltage would vary between 1.334 and 1.032 volts. With a two tank system employing multiple passes of the fluids during discharge, the voltage would gradually decrease between these limits (neglecting IR and polarization losses). With a four tank system employing only one pass of the fluids the voltage would be nearly constant but closer to the lower limit since the electrodes can only assume one potential.

Aside from reducing the capital costs of a system the two tank concept would allow greater freedom to vary the flow rate and thus the hydrodynamic environment of the electrode compartments. In this very brief description of the overall system concept the subject of the electrochemical considerations of the electrode compartments will only be eluded to rather than discussed in detail.

The ideal conceptual system would be one with two tanks employing continuous circulation of the redox fluids. The redox couples would be simple, noncomplexed and not requiring hydrogen ion participation in the half cell reactions. The membrane would preferably be a conductor of anions to the absolute exclusion of cations. Nonideal membranes would require some type of electrolyte refining process that would remove any cross diffused ions and restore them to their proper circulating loop.

#### 5. Potential Applications for Electrically

##### Rechargeable Redox Flow Cells

The primary potential application of these systems would be in the area of bulk power storage. This would encompass large installations (1000 MW/8500 MW-hr) for electric utility network peak shaving or load leveling, medium installations (10 MW/85 MW-hr) for distributed peak shaving or load leveling, and small installations (10 → 100 KW/85 → 850 KW-hr) for use in conjunction with intermittent power generation schemes (solar power, windpower, etc.). The requirement for large bulk power storage devices is being met at present by pumped hydro installations (ref. 2) where the combination of an elevated water storage pond, a hydroelectric plant/water pumping facility and a nonelevated water storage pond are required. These facilities have an attractive capital investment cost and life expectancy and thus are being built where the unique terrain requirements permit (ref. 3). The electrically rechargeable redox flow installations would be more expensive than pumped hydro facilities but would offer less restrictive terrain and capacity constraints.

The attractive features of electrically rechargeable redox flow system, as opposed to other electrochemical schemes, would be

1. Simple electrode reactions
2. Favorable exchange currents (for some redox couples)
3. No high temperatures required
4. No cycle life limitations (for the redox couples)
5. Electrochemically reversible reactions (some redox couples)

The main overall advantage of a redox flow cell as opposed to other electrochemical devices appears to be a very high overall energy efficiency. The energy densities would of course be rather low in comparison with the more usual secondary battery systems, but for the bulk power storage application overall energy efficiency is the main consideration.

#### 6. Preliminary Experimental Data

The system  $Fe^{+2}/Fe^{+3}$ , chloride ion membrane,

$Ti^{+3}/Ti^{+2}$  was selected for initial investigations. These are chloride salts with hydrochloric acid added to stabilize the titanium ion against hydrolysis. Although this pair of couples does not meet all the above listed criteria it does represent a relatively simple system. The membrane was Ionac 3475. It did not meet the criteria of preventing all cross diffusion of redox ions but served to permit electrochemical investigations to be carried out. The anode and cathode compartments employed graphitized fabric as the inert electrodes. The system was charged and discharged through a fixed resistor. Details of the cell are shown in figure 4. Approximately twenty cc of 1.0 Normal solutions served as the redox fluids. Figure 5 shows the results from a single discharge followed by a recharge. The low cell voltage was due primarily to the resistance of the membrane rather than the electrode reactions. The ampere-hours-out and the ampere-hours-in agreed quite closely with the theoretical capacity of the cell (see fig. 5). Since the projected area of the electrodes was 14 square centimeters the current density was about 50 ma/cm<sup>2</sup>. The open circuit voltage values were obtained by interrupting the discharge sequence and then reading the cell voltage with no current flow. Figure 5 illustrates several undesirable features of a redox system. The voltage vs. time (depth of discharge) relationship is not as flat as are some more conventional secondary battery systems. This is caused by the Nerstian corrections factors (-RT/nF ln Aprod/Areact) for both redox couples. The rather low open circuit voltage of the cell is the consequence of selecting couples which would be within the bounds that would preclude water electrolysis during recharge. The main causes for the low operating voltage at present are due to the high resistance of the available membrane material as well as the lack of optimization of the hydrodynamic flow conditions and electrode design of the electrode chambers. Much further work remains to bring this electrochemical concept to fruition.

#### SUMMARY AND CONCLUSION

The concept of the electrically rechargeable redox flow cell has been described mainly from a theoretical standpoint. Preliminary results from laboratory experiments point out problem areas in this concept. Thus far the contentions of high overall electrical efficiency as well as deep depths of discharge have been supported by the data. Proper membrane materials have yet to be found and more work must be done to select the best redox couples. Cost studies can then be undertaken to establish estimated costs (fixed and operating) for systems of different sizes.

#### REFERENCES

1. Amberg, E. J., "Rocky River Hydroelectric Development," Trans. AIEE, Vol. 47, Oct. 1928, pp. 1100-1109.
2. Knapp, S. R., "Pumped Storage - The Handmaiden of Nuclear Power," IEEE Spectrum, Vol. 6, No. 4, Apr. 1969, pp. 46-52.
3. The Bulletin of Arthur D. Little, Inc., Bulletin No. 503, Sept.-Oct. 1973.
4. Potter, E. C., Electrochemistry, Principles and Applications, Cleaver-Hume Press Ltd., 1956, p. 405.

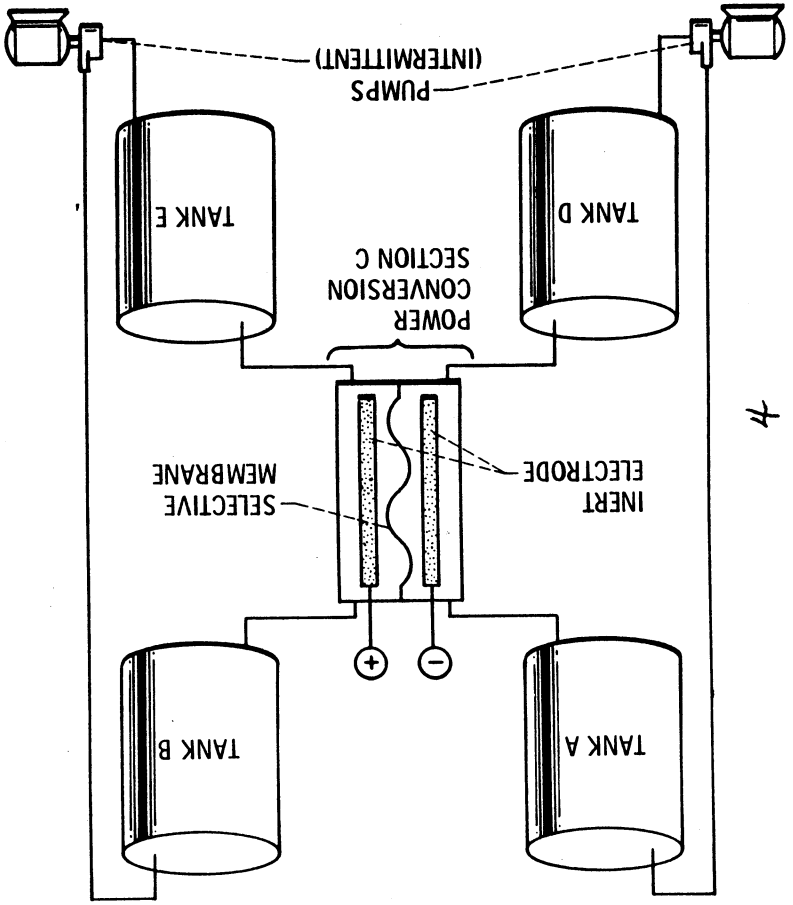


Figure 1. - Four tank electrically rechargeable redox flow cell.

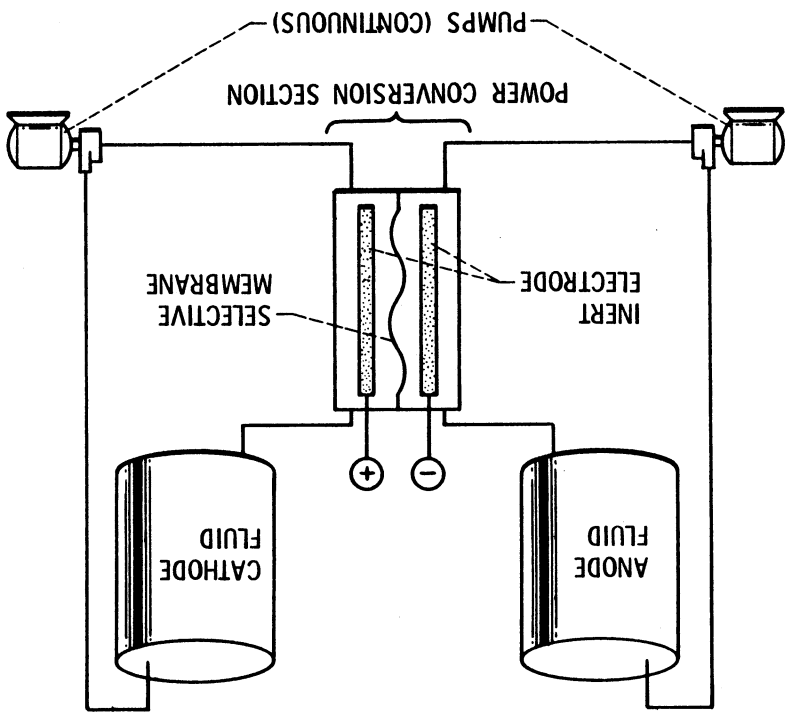


Figure 2. - Two tank electrically rechargeable redox flow cell.

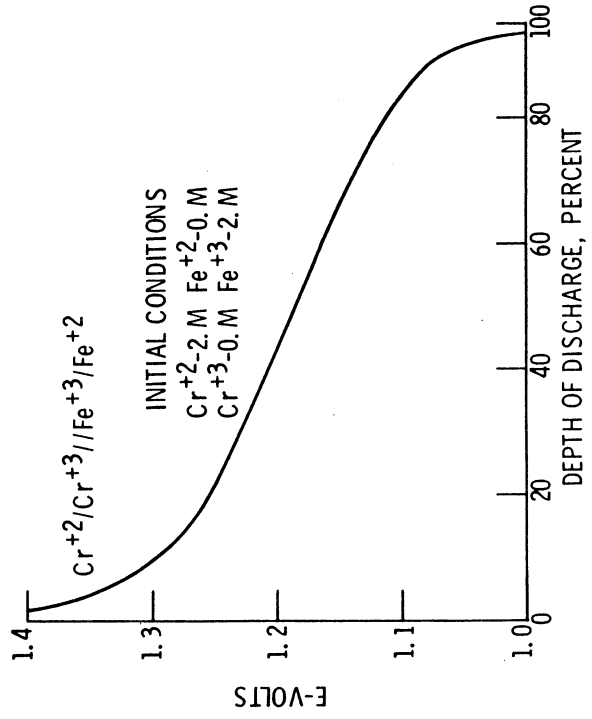


Figure 3. - Theoretical voltage vs depth of discharge for a Redox flow cell.

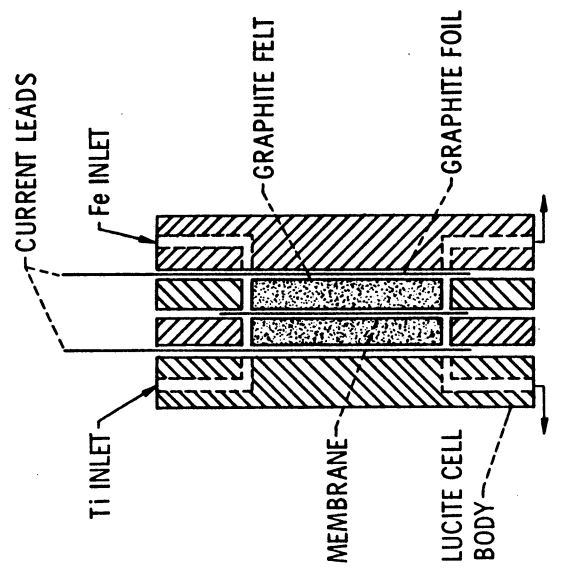


Figure 4. - Redox flow cell.

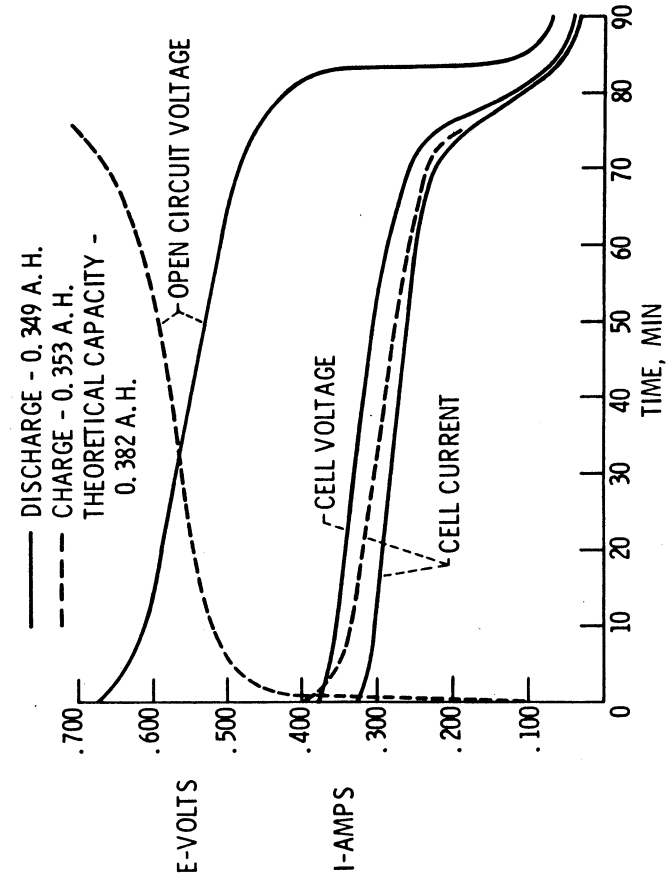


Figure 5. - Discharge/charge cycle through 1 ohm load  $FeCl_3/FeCl_2/TiCl_4/TiCl_3$ .

