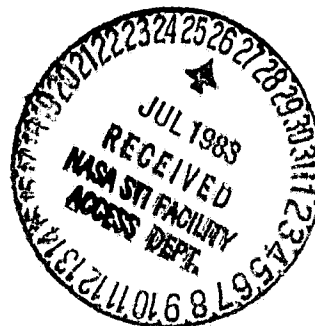


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NASA Redox Project Status Summary

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Fifth Battery and Electrochemical Contractors Conference
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ABSTRACT

This report is a summary of the results of the Redox Project effort during Cy 1982. It was presented at the Fifth U.S. Department of Energy Battery and Electrochemical Contractors Conference, Arlington, Va., Dec. 7-9, 1982.

The major development during 1982 was the shift from Redox system operation at 25° C with unmixed reactants to operation at 65° C with mixed reactants. This change has made possible a two- or three-fold increase in operating current density, to about 65 mA/cm², and an increase in reactant utilization from 40% to about 90%. Both of these improvements will lead to significant system cost reductions. Contract studies have indicated that Redox reactant costs also will be moderate. A new catalyst for the chromium electrode offers all the advantages of the conventional gold-lead catalyst while being easier to apply and more forgiving in use.

INTRODUCTION

The Redox system being developed at the NASA Lewis Research Center is based upon an acidified aqueous solution of the fully soluble chromic/chromous redox couple for the negative reactant and a similar solution of the ferric/ferrous redox couple for the positive reactant. These fluids are circulated continuously through their respective half-cells, which are typically separated by an anion exchange membrane serving to prevent cross-mixing and self-discharge of the reactant species. The inert electrodes are porous carbon or graphite felt which, in the case of the chromium half-cell, is lightly catalyzed to enhance the desired half-cell reactions while inhibiting the hydrogen evolution side reaction.

During the past year, the principal effort of the Redox Project has been to focus upon specific characteristics of the iron-chromium Redox system, including performance anomalies related to the chromium solution chemistry, performance at higher temperatures, gassing tendencies at the chromium electrode, membrane properties such as resistivity, selectivity and osmotic transfer, costs of reactants, and the effects on performance of mixing the reactants.

CHROMIUM SOLUTION CHEMISTRY

Much has been accomplished in developing an understanding of the behavior of the chromium ion species during the operation of an iron-chromium Redox cell. Puzzling performance characteristics such as poor charge acceptance rates and unavailable capacity have been explained in terms of the relative concentrations of two chromic ion species and the rates of equilibrium between the species. It has been shown that heating to 50°-65° C favors the more electrochemically active species, the monochloropentaaquochromium (III) ion (Fig. 1). Constant-voltage charge acceptance curves for a cell using a room-temperature chromium solution and a solution heated to 75° C and then quenched

back to 25° C are shown in Figure 2. (The quenching was done as an experimental convenience, to eliminate any other thermal effects, and is not an operational requirement.) At about 40% state of charge (SOC) the electrochemically active species is depleted from the untreated chromium solution, and charge acceptance quickly falls to negligible values. However, with preheated reactant, excellent charge acceptance occurs all the way to 90% SOC, and beyond. The difficulty with using room-temperature chromium reactant is further illustrated in Figure 3, which shows the concentrations of the two chromic ion species, determined by spectrophotometry, during a complete cycle. By the time 60% SOC is reached, the electrochemically active species has been consumed. Beyond this point the charge acceptance rate is limited to the rate of re-equilibration between the species, which is, at room temperature, quite slow.

FURTHER TEMPERATURE EFFECTS

Complete single-cell systems have been operated at temperatures up to 65° C. Cell resistance has been monitored as a function of temperature, state of charge, and supporting electrolyte (HCl) concentration. Polarization data for charge and discharge have been taken at various temperatures and SOC's. Depending on the system SOC and the concentration of the supporting HCl electrolyte, there is a temperature that minimizes cell resistance, giving optimum performance. Figure 4 shows the dramatic reduction in cell resistivity as temperature is increased. Another advantage of operation at high temperature is that it simplifies and reduces the cost of heat rejection from an operating system.

ELECTRODES

The primary focus of the electrode development task during the year has been to make possible the reproducible fabrication of satisfactory chromium Redox electrodes. An optimum processing temperature range has been determined to yield carbon/graphite felts which, when cleaned and catalyzed, produce electrodes having adequate chromium reduction rates and acceptably low hydrogen evolution. Completion of the current electrode work by Giner, Inc., will result in complete specifications for the preparation of carbon/graphite felt, its cleaning, and its subsequent catalyzation.

During cell testing it is occasionally noted that the gassing tendency of the chromium electrode increases with time. Experiments have shown that one cause of this phenomenon is the occurrence of ferric ion in a fully discharged chromium solution. The ferric ion apparently oxidizes the gold-lead catalyst in such a way that it subsequently cannot be restored. Such an occurrence requires a relatively specialized set of conditions and can easily be avoided. Another recently discovered cause for increased hydrogen evolution is the migration of platinum from the hydrogen electrode of a rebalance cell (an electrochemical cell used to keep the Redox reactants in balance by recombining any hydrogen evolved with the circulating ferric chloride) into the membrane of the working Redox cell. This, too, can be avoided or minimized. The encouraging thing about all this is that any increasing hydrogen evolution rate from a chromium electrode seems to result from inadvertent operational occurrences; which is to say that it is not related to any shortcoming of the electrode itself.

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Alternative chromium electrode catalysts based on bismuth are presently being evaluated and show promise. Bismuth is expected to be stable because of its relatively high reduction potential, and it also has a high hydrogen overpotential. Currently, electrodes containing these catalysts are being used in cells operating with mixed reactants at 65° C (150° F). Results of this testing are presented in a later section.

MEMBRANES

The primary goal of the membrane development program at Ionics, Inc., during the year has been to evaluate variations in the resin formulation and the substrate of the standard CDIL membrane. Improvements being sought are in the areas of membrane resistivity, selectivity, and cost. Although some of the variations have resulted in membranes that are equivalent to, or marginally better than, the CDIL standard, to date none offers the significant advances being sought.

Both the standard CDIL membrane from Ionics, Inc., and radiation-grafted anion exchange membranes from RAI Research Corp. offer a combination of resistivity and selectivity that make the basic Redox concept, which requires separation of the reactant species, feasible at room temperature. However, at 65° C, although the membrane resistivity is considerably lower, the selectivity of the present generation of membranes becomes an order of magnitude worse. Remedial treatment at the system level thus becomes necessary to prevent total cross mixing of the reactant species.

Another characteristic of all membranes so far examined is the tendency for osmotic transfer of solvent (H₂O) from one reactant solution to the other. Experimental work has defined the respective reactant solution concentrations which will result in a more or less isotonic situation, i.e., one in which the tendency toward osmotic transfer is nullified. For example, at room temperature the use of 1.1 M FeCl₂ and 0.9 M CrCl₃ in 1.0 N HCl has been shown in some tests to effectively halt solvent transfer. However, for reasons not yet fully understood, this approach is not always successful; and when it fails, some system-level method of reactant solution refurbishment becomes necessary.

OPERATION WITH MIXED REACTANT SOLUTIONS

The current absence of a "perfect" membrane, that is, one which allows free passage of chloride and hydrogen ions yet holds to a minimal level the transfer of iron and chromium ions, has led to a serious evaluation of the mixed reactant mode of operation. As the name implies, in this concept both reactant solutions, in the discharged state, consist of 1 M FeCl₂ and 1 M CrCl₃, acidified with HCl. Operation of a Redox system with such totally premixed reactants offers several advantages over the standard approach of using a highly selective membrane to keep the reactant solutions separate. Membranes will be needed only to retard the convective transfer of reactant volume and thus can be very open in structure or be of a microporous construction. Such membranes will have a very low resistivity, with an attendant improvement in cell voltage efficiency; their cost should also be quite low. Any solvent transfer, or any reactant imbalance resulting from a net migration of reactant species from one side to the other, is easily countered simply by reblending the reactant solutions while discharged and then repartitioning them to their respective tanks.

The disadvantages associated with the mixed reactant concept are a reduced coulombic efficiency, due to easier cross diffusion and subsequent self-discharge of the reactant species; a reduction of open-circuit voltage of about 50-70 mV at each state of charge, due to the diluting effect of the cross-mixed reactant species; and an increased expense for reactants. The latter subject is discussed later.

Initial evaluation of the mixed reactant concept has been very encouraging. Tests have been carried out with 14.5-cm² cells at 65° C, using a cation exchange membrane known to have both low resistivity and very poor selectivity. This is a radiation-grafted membrane designated ML-21, supplied by RAI. Constant-current charge and discharge data for a typical cycle are shown in Figure 5. Some of the more notable characteristics are as follows:

(1) Because of the low cell resistivity, operation at a much higher current density than previously considered feasible, is possible. This will translate into lower cell and stack costs and, because reduced membrane area, a partial recovery of the coulombic efficiency losses associated with the more open membrane.

(2) The coulombic efficiency of 92% and the associated energy efficiency of 72% at a current density of 64.5 mA/cm² are especially attractive in light of the fact that no attempt at membrane optimization has occurred yet.

(3) Nearly the complete theoretical capacity (87%) is utilized, because of the operation at elevated temperature.

(4) The hydrogen evolution rate is low.

(5) As attractive as the cell resistivity is at 1.8 ohm-cm², it includes a cell blank of about 1.4 ohm-cm² which is mostly terminal effect. In other words, an interior cell of a bipolar stack can easily be expected to have a resistivity of 0.7 ohm-cm² or less.

(6) After three months operation there is no discernible deterioration of the membranes.

A very similar set of data is presented in Figure 6. The only significant difference in this test is that the chromium electrode is catalyzed with the bismuth-based material mentioned earlier, instead of the standard gold-lead alloy. The electrochemical performance of the two catalysts is identical at 65° C, and the rate of hydrogen evolution from the bismuth-based catalyst is somewhat less than for the gold-lead material.

Polarization data for this cell, taken at 50% SOC, are presented in Figure 7. The linearity of the curves indicates that the only polarization is due to cell resistance. It is significant that the reblending of the reactant solutions three times in order to counter solvent transfer had no measurable effect on cell performance.

All the above data, though quite preliminary, already give strong corroboration to the anticipated benefits of operation with mixed reactants.

REACTANT COST STUDIES

During the past year, two contract efforts have been carried out to estimate the sales price of Redox system reactants when produced at a rate of 25 000 tons/annum of contained chromium. These studies were performed by Allied Chemical, a major producer of chromium chemicals, and Charles River Associates, a consulting firm knowledgeable in hydrometallurgical processes. Several production paths were examined, each starting with either chromite ore, ferrochrome, or the intermediate, sodium chromate. The projected prices, which include 30% return on investment, are for the complete reactant package, consisting of 1 M CrCl_3 in 1.0 N HCl and 1 M FeCl_2 in 1.0 N HCl. The projected prices ranged from 23 to 53 cents per pound of contained $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. In Table 1 the production routes examined by each contractor are listed along with the resultant reactant costs, expressed in dollars per kilowatt hour. These costs are presented for both the unmixed and the mixed reactant concepts. All of these cost projections are quite attractive relative to previous estimates, and they indicate that the cost penalty associated with the mixed reactant concept is not prohibitive.

CONCLUDING REMARKS

The flow of the Redox project during the past year has been inexorably toward a serious evaluation of the mixed reactant mode of operation. First of all, the analysis of the operating difficulties related to the chromium reactant solution chemistry revealed that operation at temperatures around 65° C was imperative. At such temperatures the difficulties were virtually eliminated. However, the selectivities of all membranes deemed adequate at room temperature were greatly impaired at the higher temperatures, thus allowing a much greater rate of reactant cross mixing. Although this could be countered by periodically refurbishing the reactant solutions, the associated expense and system complexity militate against it. All these factors, plus the cost of "selective" membranes and the tendency of all membranes to permit osmotic solvent transfer, at last led to the decision that the use of mixed reactants must be examined.

Experimental evaluation of this concept has been very encouraging both in terms of single-cell performance and the operational ease of dealing with solvent transfer and/or reactant cross diffusion. Additional encouragement has come from reactant cost studies that indicate that the cost penalty due to the additional requirement for reactants is not excessive.

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TABLE I. - REDOX REACTANT COST PROJECTION, BASED ON 25 000 TONS PER YEAR OF CONTAINED CHROMIUM (1 M CrCl₃, 1 M FeCl₂, 1 N HCl; 30% ROI)

	Unmixed reactants ^a	Mixed reactants ^b
	Cost, \$/kWh	
Allied Chemical Corp.		
Reductive chlorination of chromite ore	21.73	32.60
Electrolytic reduction of sodium chromate	17.02	25.53
Methanol reduction of sodium chromate	14.00	21.00
Chlorination of prereduced ore	11.31	16.97
Charles River Associates		
Reductive chlorination of chromite ore	12.27	18.41
Hydrometallurgical dissolution of chromite ore	10.74	16.11
Hydrometallurgical dissolution of ferrochrome	9.21	13.82

^a1.67 times the stoichiometric requirement.

^b2.50 times the stoichiometric requirement.

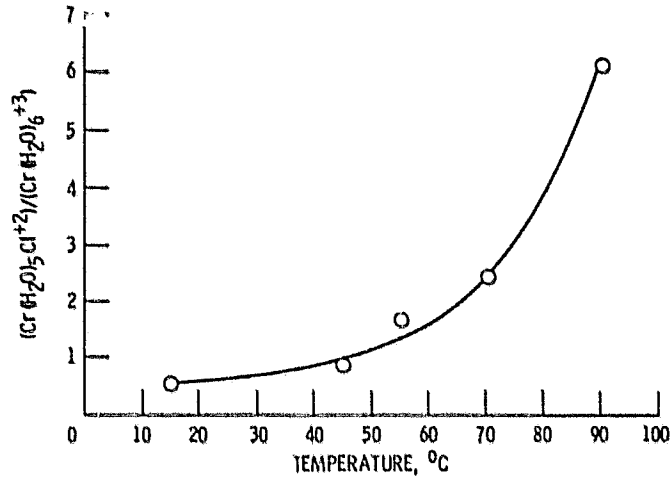


Figure 1. - Chromic ion concentration ratio as a function of temperature.

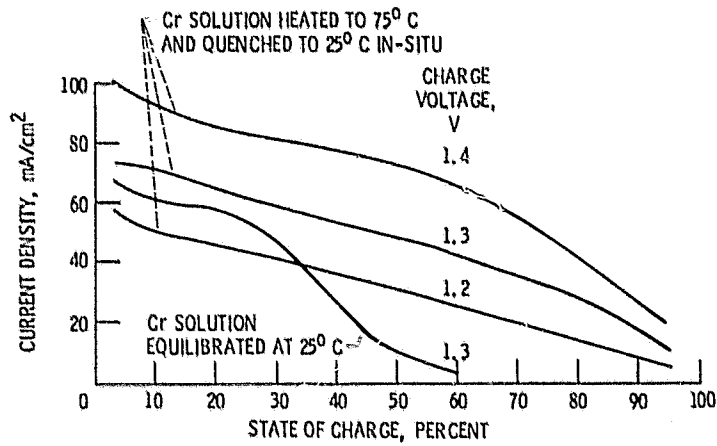


Figure 2. - Constant-voltage charge acceptance rate as a function of state of charge.

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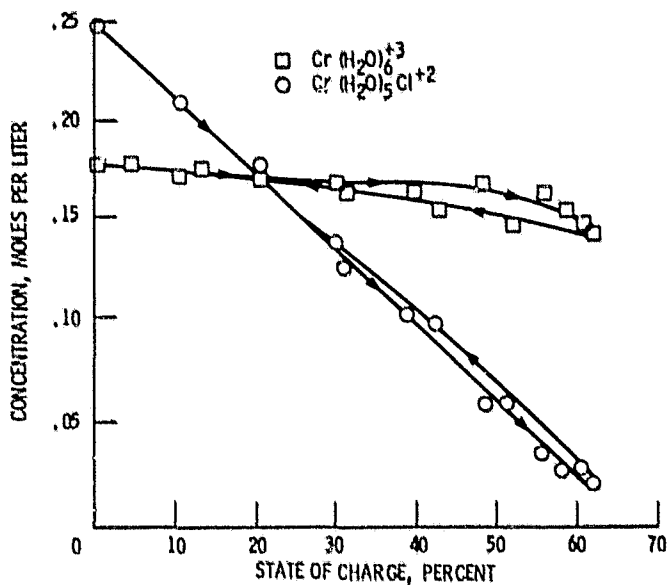


Figure 3. - Concentrations of chromic ion species during a charge-discharge cycle.

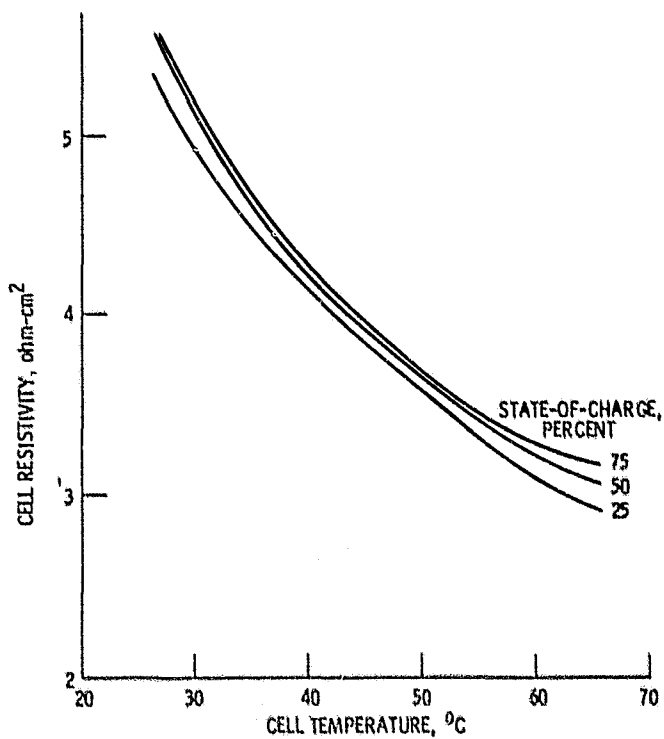


Figure 4. - Redox cell resistivity as a function of temperature for CDIL membrane.

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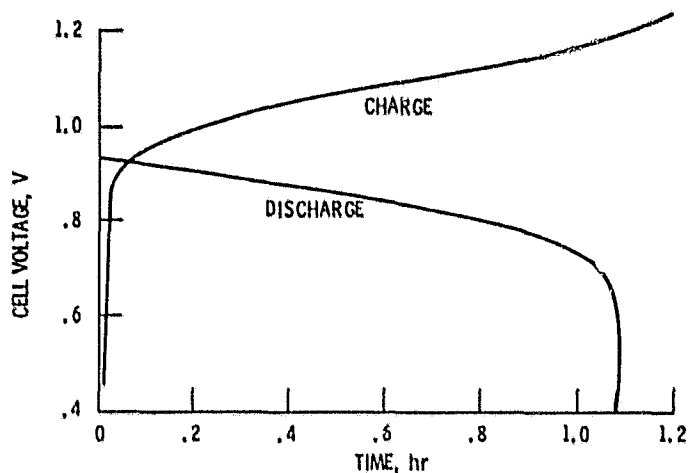


Figure 5. - Constant-current charge and discharge performance with mixed reactants at 65° C - gold-lead catalyst. Current density, 64.5 mA cm²; mixed reactants (fully discharged: 1.1 M FeCl₂, 0.9 M CrCl₃, 2.0 N HCl); cation exchange membrane; state of charge, 0 to 87 percent; operating temperature, 65° C; energy efficiency, 72.3 percent; coulombic efficiency, 92.2 percent; voltage efficiency, 78.4 percent; hydrogen evolution, 0.9 percent of charge capacity; cell resistivity, 1.76 ohm-cm²; membrane resistivity, 0.36 ohm-cm².

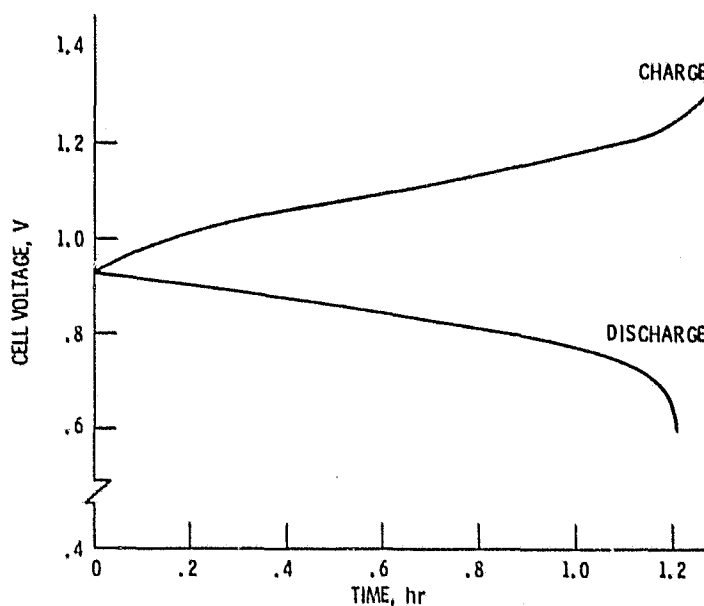


Figure 6. - Constant-current charge and discharge performance with mixed reactants at 65° C - nonnoble metal catalyst. Current density, 64.5 mA cm²; mixed reactants (fully discharged: 1.0 M FeCl₂, 1.0 M CrCl₃, 3.0 N HCl); cation exchange membrane; state of charge, 0 to 87 percent; operating temperature, 65° C; energy efficiency, 73.1 percent; coulombic efficiency, 94.6 percent; voltage efficiency, 77.2 percent; hydrogen evolution, 0.2 percent of charge capacity; cell resistivity, 1.74 ohm-cm²; membrane resistivity, 0.34 ohm-cm².

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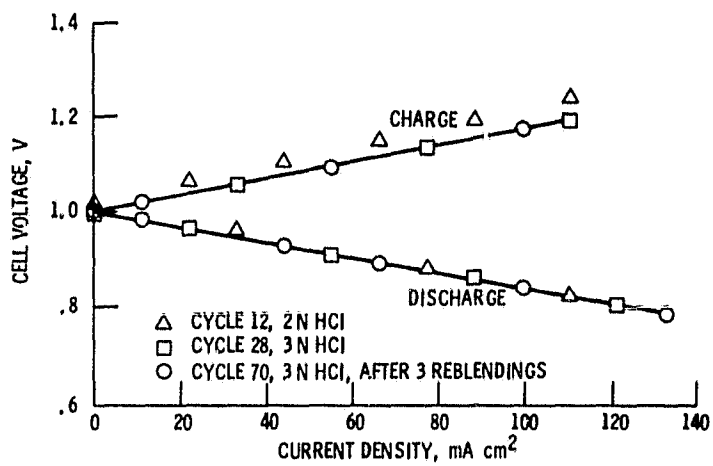


Figure 7. - Polarization data; Mixed reactants (Fully discharged; 1.1 M FeCl₂, 0.9 M CrCl₃); cation exchange membrane; nonnoble chromium electrode catalyst; operating temperature, 65° C; state of charge, 50 percent.